



Review of research on Plitvice Lakes, Croatia in the fields of meteorology, climatology, hydrology, hydrogeochemistry and physical limnology

Zvezdana Bencetić Klaić¹, Josip Rubinić² and Sanja Kapelj³

¹Department of Geophysics, Faculty of Science, University of Zagreb

²Faculty of Civil Engineering, University of Rijeka

³Faculty of Geotechnical Engineering, University of Zagreb

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In lakes, several physical, chemical, and biological processes occur simultaneously, and these processes are interconnected. Therefore, the investigation of lakes requires a multidisciplinary approach that includes physics (including the physics of the atmosphere, *i.e.*, meteorology), chemistry, geology, hydrogeology, hydrology and biology. Each of these disciplines addresses a lake from a different point of view. However, lake studies that primarily belong to one field, at least to some extent, report their findings in ways that are associated with other fields; this type of reporting is caused by the inherent interconnections between phenomena from different disciplines. Plitvice Lakes, Croatia, are composed of a unique cascading chain of karst lakes, and these lakes have been investigated by numerous authors. Here, we provide an overview of the studies of the Plitvice Lakes Area (PLA) that address meteorology, climatology, hydrology, hydrogeochemistry and physical limnology. Our aim is to synthesize the results from each of these disciplines and make them available to scientists from other related disciplines; thus, this review will facilitate further investigations of the PLA within the natural sciences. In addition, valuable results from early investigations of Plitvice Lakes are generally unavailable to the broader scientific community, and are written in Croatian. Here, we summarize these results and make them available to a wider audience.

Keywords: catchment, geosciences, hydrodynamics, karst, tufa barriers

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List of acronyms and abbreviations

ASL	Above Sea Level
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CFCs	Chlorofluorocarbons
DIC	Dissolved Inorganic Carbon
DM	Dispersion Model
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
E	Eastern
EM	Exponential Model
GIS	Geographic Information System
GPS	Global Position System
LAS	Linear Alkylbenzene Sulphonates
LM	Linear Model
LPMs	Lumped Parameter Models
LST	Local Standard Time
MHS	Meteorological and Hydrological Service of Croatia
MRT	Mean Residence Time
N	Northern
NE	Northeastern
NW	Northwestern
OM	Organic Matter
PAHs	Polycyclic Aromatic Hydrocarbons
PEC	Probable Effect Concentration
PFM	Piston Flow Model
PFMDM	Piston Flow Model-Dispersion Model
PFMEM	Piston Flow Model-Exponential Model
PLA	Plitvice Lakes Area
PLNP	Plitvice Lakes National Park
PIM	Particulate Inorganic Matter
POM	Particulate Organic Matter
SE	Southeastern
S	Southern
SW	Southwestern
TSM	Total Suspended Matter
VSMOW	Vienna Standard Mean Ocean Water
W	Western

1. Introduction

In the past, the Plitvice Lakes (in Croatian, *Plitvička jezera*) were called the Devil's Garden (Franić, 1910). Known for their beauty and geomorphologic uniqueness associated with the biodynamic processes of tufa formation, the Plitvice Lakes were the first national park established in Croatia, *i.e.*, the “Plitvice Lakes National Park” (in Croatian, *Nacionalni park Plitvička jezera*, hereafter PLNP) was established in 1949. The PLNP extends over 294.82 km² (UNESCO, 2017), and the total lake surface area corresponds to approximately 1.949 km² (Babinka, 2008). The total water volume, according to Gavazzi (1919) and Babinka (2008), has been estimated to be approximately 25.87 and 22.95 million cubic meters, respectively. In 1979, the PLNP was added to the United Nations Educational, Scientific and Cultural Organization (UNESCO) World Heritage register, and it is the only natural site that belongs solely to Croatia¹ (UNESCO, 2017). The PLNP is situated in the inland mountainous area of Croatia at altitudes between 450 and 1280 m. It is located between the mountains Mala Kapela (1280 m), Lička Plješivica (1640 m) and Medvedak (884 m), *i.e.*, between the latitudes 44°44'34" N and 44°57'48" N and longitudes 15°27'32" E and 15°42'23" E (Babinka, 2007; NPPL, 2007).

In total, the chain of 16 lakes is approximately 9 km long and is located in a forested karst environment (Fig. 1). At higher altitudes, beech-fir forest is found, while beech forest is dominant in the areas adjacent to the lakes. The lakes descend from 637 m above sea level (hereafter ASL) in the south to 475 m ASL in the north (Meaški, 2011), and they are interconnected with cascades and waterfalls. They are grouped into 12 Upper Lakes (in Croatian *Gornja jezera*, lakes 1–12 in Tab. 1) and 4 Lower Lakes (in Croatian *Donja jezera*, lakes 13–16 in Tab. 1). The highest, southernmost Prošće Lake is fed from the south and west by the Matica River (which is mainly produced by the confluence of the *Bijela rijeka* and *Crna rijeka* springs, while additional, smaller inflow originates from Kavga, Pećina, and Ljeskovac sources, and a few weak, intermittent sources) and Sušanjski spring, respectively. Downstream of the lakes, below the Sastavci waterfall, the Korana River starts. The Upper Lakes are mostly built on a Triassic low permeable dolomite base that forms a hydrogeological barrier, while the Lower Lakes and the Korana River canyon are on highly permeable upper Cretaceous limestone bedrock (Polšak et al., 1967; Polšak, 1969; Velić et al., 1970). At the most upstream portion of the Korana River, the initiation of tufa formation processes

¹ In total, 10 sites are associated with Croatia, and the three of them are transboundary (one natural – Primeval Beech Forests of the Carpathians, and two cultural – *Stećci* Medieval Tombstones Graveyards and Venetian Works of Defence). Among the seven sites belonging solely to Croatia, six are cultural (the Episcopal Complex of Euphrasian Basilica in Poreč, the Cathedral of St. James in Šibenik, the Historic City of Trogir, the Historical Complex of Split with the Palace of Diocletian, Stari Grad Plain in Hvar Island, and the Old City of Dubrovnik), while Plitvice Lakes National Park is the only natural site (UNESCO, 2017).

and the establishment of new tufa barriers, *i.e.*, the initiation of the genesis of new lake systems, is found. Moreover, the same portion of the Korana River is characterized by significant underground water loss from the riverbed downstream of the Korana Bridge (Rubinić et al., 2008).

One of the most unique and valuable characteristics of Plitvice Lakes is the tufa formation and the consequent creation of barriers that divide the lake chain into individual lakes. The processes involved in the formation, maintenance and growth of tufa barriers (Pevalek², 1924, 1935, 1938) strongly depend on the fragile composition of the physical, chemical and biological conditions in the lakes. This formation process occurs within a very narrow range of water temperatures, under specific chemical conditions of the water flowing over barriers, and under the presence of specific aquatic primary producers (*i.e.*, algae, bacteria and moss). Moreover, it generally depends on the quantity of flowing water and the water velocity (*e.g.*, Pavletić, 1957; Matoničkin and Pavletić, 1960; Kempe and Emeis, 1985; Srdoč et al., 1985; Chafetz et al., 1994; Špoljar et al., 2011). Therefore, this sensitive biodynamic process and the preservation of Plitvice Lakes can easily be endangered by human activity. This threat was recognized long ago by Roglić (1951) and Petrik (1961), who identified possible lake eutrophication due to the development of tourism and the consequent increase in waste production. A few decades later, Böhm (1997) listed a number of already observed negative effects from the intense development of tourism in the area, such as the construction of roads passing through the PLNP. Since this was a main road from the inland area to the coast, it was laden with heavy traffic; consequently, this roadway contributed to the pollution of the PLA, which included lead, nitrogen oxides, and photochemical pollutants. Another problem was the increased construction of new hotels and other buildings, which was accompanied by shortages in drinking water and the lack of a proper sewage system. Simultaneously, the number of tourists was increasing. For example, during the period of 1970-1990, up to 900,000 tourists visited the PLNP each year; furthermore, on Sundays and national holidays during the summer season, the daily number of visitors was as high as 10,000. Moreover, in the last decade, the number of visitors has been even higher. For example, in 2017, the total number of visitors was 1,720,331, while the daily maximum number of visitors was 16,125 (NPPL, 2018). According to Božičević et al. (2013), the reconstruction of the water supply and sewage systems, as well as the restriction in the number of daily or monthly visitors to the NPPJ is still needed to preserve this valuable area.

In the past, the creation and disappearance of individual lakes in the Plitvice Lakes Area (hereafter, PLA) was affected by human interventions. During the 18th and 19th centuries, mills, sawmills and corresponding canals were built.

² Ivo Pevalek (1893–1967), Croatian botanist praised for the legal protection of Plitvice Lakes. A research unit of PLNP, which was founded in 1961, was named after him in 1975, as the “Ivo Pevalek Scientific Research Center”.

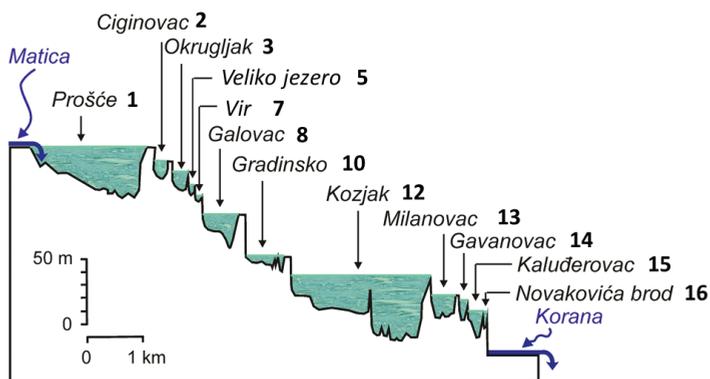


Figure. 1 Approximately south (left)–north (right) cross-section of Plitvice Lakes (adopted from Rubinić et al., 2008). The cross-section shows only 12 lakes, while all 16 lakes are listed in Tab. 1.

Thus, the course of water was changed, and the area was drained. Tufa was also used as a building material, which resulted in lowering some barriers by several meters. Further, younger barriers were mechanically damaged by timber floating for commercial purposes. Accordingly, approximately 10 to 20 lakes disappeared (e.g., in the past, there were 8 to 9 lakes solely in the valley of *Bijela rijeka*). Anthropogenic influences were the strongest in the southern populated area, where the villages of Babin Potok and Plitvički Ljeskovac were founded (Franić, 1910; Markowska, 2004). While logging and sawmill industries were phased out completely by the early 1960s (e.g., Babinka, 2007), currently, the Plitvice Lakes are endangered by both intense tourism in the area and different, new, globally present threats. During the past several decades, the anthropogenic pressure on aquatic systems has increased worldwide due to the increase in population and the consequent economic growth and higher water demands (e.g., Gude, 2017), pollution (e.g., Amiri et al., 2014), land use change (e.g., Baier et al., 2014), and hydrological disturbance caused by dams (e.g., Janse et al., 2015). Moreover, global warming imposes additional pressure on aquatic systems since the anticipated climatic change may lead to changes in the hydrological regime (e.g., Rubinić et al., 2011; Shresta et al., 2014) and may further exacerbate water quality problems in the future (e.g., Diamantini et al., 2018). In light of this information, recent research of the Plitvice Lakes (Rubinić et al., 2008; Rubinić and Zwicker Kompar, 2011; Bonacci, 2013a) has already indicated there has been variability in the dynamics of tufa barrier growth over the last several decades, and there has been a very prominent, decreasing trend in the mean annual flow through the lakes system. Since the Plitvice Lakes geographically belong to a region that has been affected by climatic change, e.g., an increase in temperature and a decrease in wintertime precipitation is expected (e.g., Bulić et al., 2012; Herceg-Bulić, 2012), the water quality and the tufa growth dynamics might be affected in the future.

There are numerous studies of the PLA that have focused on a wide variety of topics within the field of natural sciences (Sliepčević and Krajcar Bronić, 2001). Early investigations addressed the geology and geomorphology of the area, tufa barrier formation, and geological predispositions for tufa formation (Franić, 1910; Gavazzi, 1904, 1919; Koch, 1916, 1926, 1932; Roglić, 1951, 1974). Herak (1962) studied the tectonics of the greater area, while the most detailed investigations of the geological and hydrogeological characteristics of the PLA were conducted by Polšak (1959, 1960, 1962, 1963, 1964, 1965, 1974); moreover, research on the speleological phenomena within the PLA was studied by Božičević (1969, 1971, 1973, 1991). There have also been numerous hydrobiological/ecological studies of the PLA (*e.g.*, Emili, 1958, 1965; Matoničkin and Pavletić, 1963). Some of the more recent studies have addressed the water supply of the PLA (Kapelj et al., 2003; Pavičić et al., 2006, 2007), as well as groundwater protection, natural vulnerability maps and risk assessments related to the surface and subsurface water resources (Kapelj et al., 2004, 2007, 2013). Here, we focus on past investigations of the Plitvice Lakes that are relevant for understanding the physical and hydrogeochemical processes and conditions of this unique lakes system.

2. Lake morphometries

The first chart that depicted the Plitvice Lakes as a single, nameless lake was drawn by a cartographer, Gerhard Mercator, in the 16th century, while a chart from 1664 displays four nameless lakes positioned southwest of the headwaters of the Korana River. The name *Plitivička jezera* was first introduced by a parson, Dominik Vukasović in 1777, based on the Croatian term for a shallow basin (*pličina* or *plitvak*). Vukasović described *Plitvica* as ‘five nice lakes in the most dense forest on the Turkish border, where in any time, the nicest and the best trout are caught’ (Franić, 1910). Measurements of the lakes’ depths that were conducted by the major Franz (Franjo) Bach in 1850 are considered as the first limnological study of the Plitvice Lakes³ (NPPL, 2017), while Franić⁴ (1910)

³This first limnological study was accompanied by the geological survey by Dr. Josip Sauch, and it was followed by other studies of Plitvice. Botanical investigations were performed by Josip Schlosser and Ljudevit Vukotinović (whose original family name was Farkaš), while zoological studies were conducted by Dragutin *pl.* Šoštarić (NPPL, 2017). It is interesting that, by profession, Schlosser was a physician, while Vukotinović graduated in law, and for a certain period worked as a court judge. He was also a poet, short story writer and dramatist, and a member of the Croatian Parliament. Apart from botany, Vukotinović also studied mineralogy. He was the one of the first sixteen full members of the Yugoslav (currently Croatian) Academy of Science (PROLEKSIS, 2013), where he was elected in 1867.

⁴Dragutin Franić (1864–1924) was a geographer and a high-school professor educated at the universities of Zagreb and Vienna. He published approximately 50 professional papers in periodicals (Piškorić, 1995) and a travel book, *Putovanje s gacima* (Franić, around 1901).

was the first to calculate the lakes' surface areas using cadastral and geographical maps at the 1:25,000 scale (Petrik, 1958).

Gavazzi (1919), who performed the first comprehensive limnological study of Plitvice Lakes, reported on the lakes' relative altitudes (*i.e.*, the height differences between each set of two adjacent lakes), absolute altitudes, areas and volumes (Tab. 1). However, Gavazzi emphasized that the absolute heights (*i.e.*,

Table 1. List of 16 Plitvice lakes (NPPL, 2017). Data taken from Franić (1910), Gavazzi (1919), Petrik (1958), Babinka (2007, 2008), Wikipedia (2015) and NPPL (2017) are denoted by the superscripts F , G , P , B , W and N , respectively. UL and LL denote the Upper Lakes and Lower Lakes, respectively. Names listed out of parentheses in bold are those used by the NPPL (2017). In parentheses are the name variants used in other sources. To avoid confusion regarding the lake names, Petrik (1958) used the names that corresponded to the geodetic survey from 1940 (these are underlined in the present table), although for some lakes, he suggested other variants as more appropriate (these are italic in the present table). The superscript P^ denotes the absolute lake heights for August 1951, while $P^\&$ corresponds to the absolute lake heights for 16 September 1952 (Petrik, 1958).*

Lake code	Lake name	Altitude (m)	Area (ha)	Depth (m)	Volume (km ³)	Comment
1	Prošćansko jezero (Prošće, Prošćanski)	636.51 ^G 636 ^{N,W} 639 ^F 636.66 ^{P*} 636.54 ^{P&} 636.60 ^B	68.09 ^G 68.0 ^W 68.21 ^F 68.272 ^P 68.20 ^B	37 ^{N,W} 40.3 ^G (max) 13.2 ^G (avg) 37.4 ^P (max) 37.4 ^B (max)	0.00899 ^G 0.00767 ^B	UL
2	Ciginovac (Cigino, Ciganovac)	625.28 ^G 620 ^W 623.29 ^{P*} 620.51 ^{P&} 625.60 ^B	7.08 ^G 7.5 ^W 7.548 ^P 7.50 ^B	11 ^W 13.4 ^G (max) 6.8 ^G (avg) 11.1 ^P (max) 11.10 ^B (max)	0.00033 ^G 0.00047 ^B	UL
3	Okrugljak (Okrugljak g., Okruglič, Okrugljak gornji, Kruginovac, Okrugljaj)	613.15 ^G 613 ^W 613.03 ^{P*} 613.60 ^{P&} 613.60 ^B	4.89 ^G 4.1 ^W 4.132 ^P 4.10 ^B	15 ^W 10.3 ^G (max) 5.3 ^G (avg) 15.3 ^P (max) 15.30 ^B (max)	0.00032 ^G 0.00019 ^B	UL
4	Batinovac (Bakinovac, Batin)	610.03 ^G 610 ^W 610.03 ^{P*} 610.13 ^{P&} 610.10 ^B	0.47 ^G 1.48 ^G 1.5 ^W 1.528 ^P 1.50 ^B	5 ^W 5.9 ^G (max, Lower Bakinovac) 3.2 ^G (avg, Lower Bakinovac) 5.5 ^P (max) 5.50 ^B (max)	0.00004 ^G (Donji Bakinovac) 0.00004 ^B	UL Gavazzi (1919) distinguishes two lakes, the Upper and the Lower Batinovac, with areas of 0.47 and 1.48 ha, respectively.
5	Veliko jezero (Crno jezero)	607.56 ^G 607 ^W 607.68 ^{P*} 607.51 ^{P&} 607.50 ^B	1.96 ^G 1.5 ^W 1.692 ^P 2.00 ^B	8 ^W 6.0 ^G (max) 3.2 ^G (avg) 8.1 ^P (max) 8.10 ^B (max)	0.00006 ^G 0.00005 ^B	UL

Table 1. Continued.

Lake code	Lake name	Altitude (m)	Area (ha)	Depth (m)	Volume (km ³)	Comment
6	Malo jezero (Jovinovac)	605.37 ^G	1.11 ^G	10 ^W	0.00005 ^G	UL
		605 ^W	2.0 ^W	9.6 ^G (max)	0.00003 ^B	
		605.82 ^{P*}	1.042 ^P	4.2 ^G (avg)		
		605.64 ^{P&}	2.00 ^B	10.0 ^P (max)		
		605.60 ^B		9.00 ^B (max)		
7	Vir	598 ^W	0.41 ^G	4 ^W	0.000007 ^B	UL Altitude not reported in Gavazzi (1919).
		598.52 ^{P*}	0.6 ^W	4.4 ^P (max)		
		598.72 ^{P&}	0.600 ^P	5.00 ^B (max)		
		598.70 ^B	0.60 ^B			
8	Galovac	584.44 ^G	12.54 ^G	24 ^W	0.00117 ^G	UL
		582 ^W	12.5 ^W	23.6 ^G (max)	0.00108 ^B	
		584.79 ^{P*}	12.540 ^P	11.2 ^G (avg)		
		584.56 ^{P&}	12.50 ^B	24.4 ^P (max)		
		584.60 ^B		24.40 ^B (max)		
9	Milino jezero (Milino jezerce, Milinovo jezero)	564.76 ^G	0.13 ^G	1 ^W		UL Petrik (1958) does not report the lake area.
		564 ^W	1.0 ^W			
10	<i>Gradinsko jezero</i> (Jezerac, Gradinsko jezerce, Buk, Burget, Jezerce, Gradinovac)	552.97 ^G	7.55 ^G	10 ^W	0.00016 ^G	UL Petrik (1958) gives the total area of both lakes, <i>i.e.</i> , 8.094 ha. UL
		553 ^W	8.1 ^W	7.0 ^G (max)	0.00026 ^B	
		553.32 ^{P*}	8.10 ^B	3.0 ^G (avg)		
		553.24 ^{P&}		10.0 ^P (max)		
		553.00 ^B		10.00 ^B (max)		
11	Burgeti (Burgetići)	552.89 ^G	0.67 ^G	2 ^W	0.00004 ^G	
		545 ^W	0.1 ^W	8.4 ^G (max) 3.7 ^G (avg)		
12	<i>Kozjak</i> (Kozje jezero)	534.88 ^G	82.60 ^G	46 ^{N, W}	0.01425 ^G	UL Only the lake area (without the area of the island).
		534 ^{N, W}	81.5 ^W	49.4 ^G (max)	0.01271 ^B	
		534.99 ^{P&}	81.506 ^{P*}	17.3 ^G (avg)		
		535.00 ^B	82.00 ^B	46.4 ^P (max)		
				46.40 ^B (max)		
13	<i>Milanovac</i> (<i>Milanovo jezero</i> , Milovano jezero, Milinovac)	523.12 ^G	3.37 ^G	18 ^W	0.00030 ^G	LL
		523 ^W	3.2 ^W	18.0 ^G (max)	0.00031 ^B	
		523.38 ^{P*}	3.252 ^P	8.3 ^G (avg)		
		523.33 ^{P&}	3.20 ^B	18.4 ^P (max)		
		523.30 ^B		18.40 ^B (max)		
14	<i>Gavanovac</i> (<i>Gavanovo jezero</i> , Okrugljak d., Okrugljak donji, Osredak)	514.22 ^G	0.74 ^G	10 ^W	0.00003 ^G	LL
		514 ^W	1.0 ^W	10.0 ^G (max)	0.00003 ^B	
		514.55 ^{P*}	0.656 ^P	4.5 ^G (avg)		
		514.57 ^{P&}	0.70 ^B	10.2 ^P (max)		
		519.00 ^B		10.00 ^B (max)		
15	<i>Kaluđerovac jezero</i>	504.95 ^G	2.02 ^G	13 ^W	0.00013 ^G	LL
		505 ^W	2.1 ^W	14.5 ^G (max)	0.00011 ^B	
		505.16 ^{P*}	2.100 ^P	7.2 ^G (avg)		
		505.23 ^{P&}	2.10 ^B	13.4 ^P (max)		
		505.20 ^B		13.40 ^B (max)		
16	<i>Novakovića brod</i> (Kravlji brod, Nukovića brod)	503.03 ^G	0.54 ^G	3 ^W	0.000004 ^B	LL
		503 ^W	0.4 ^W	3.8 ^P (max)		
		502.79 ^{P*}	0.404 ^G	4.50 ^B		
		502.82 ^{P&}	0.40 ^B			
		503.00 ^B				

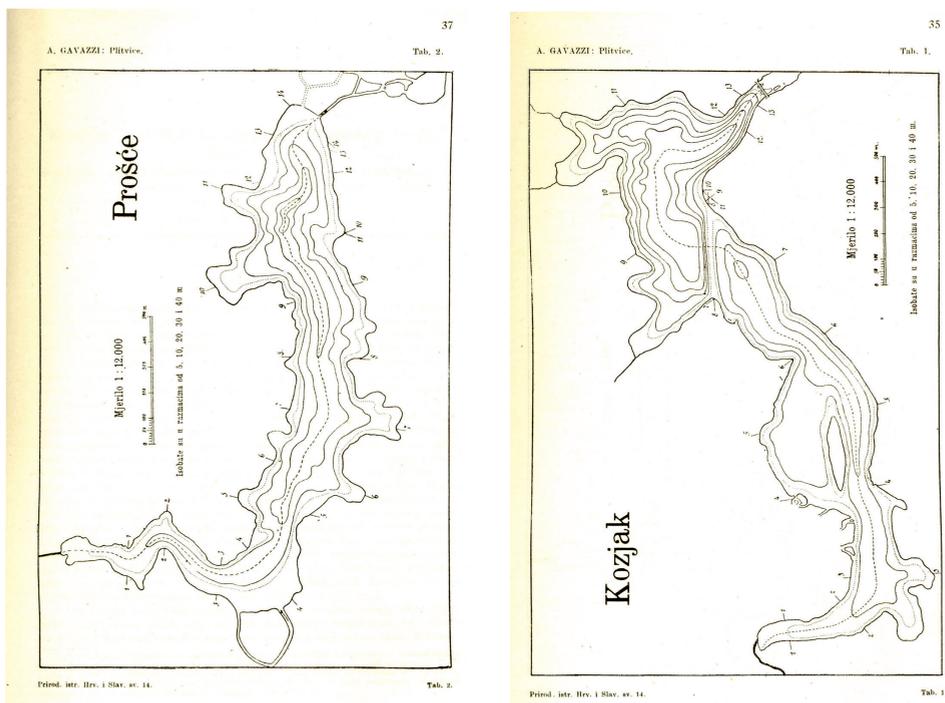


Figure 2. Bathymetry of the Lake 1 (left) and the Lake 12 (right) as given by Gavazzi (1919).

altitudes in Tab. 1) were determined under low water levels and with no available hydrometer measurements. Additionally, Gavazzi made bathymetric maps for the lakes 1 and 12 (Fig. 2).

During a multiyear (1951–1954) observational study of Plitvice Lakes that was financed by the PLNP, Petrik (1958) performed approximately 5400 measurements of lake depths, and afterwards, based on interpolation, constructed isobaths for the lakes. Examples depicting lakes 6 and 10 are shown in Fig. 3. Petrik also showed in detail the submerged barriers that are found in lakes 6 and 12. Additionally, the author reported on the absolute lake heights, maximum lake depths, areas and volumes (Tab. 1). To determine the lake areas, Petrik employed a geodetic survey from 1940 at the scale 1 : 2,500. Babinka later recalculated Petrik's lake volumes (Babinka, 2007) by assuming that his bathymetry was correct but his volumes were inaccurate (Tab. 1).

Petrik (1958) addressed the differences between his data and data provided by Franić (1910) and Gavazzi (1919), which he attributed to the quick changes that occur in lakes. As an illustration of these quick changes, Petrik described the Lake 10 (Gradinsko), for which the water level changes were very high during the period 1951–1953. This resulted in substantial temporal changes in the

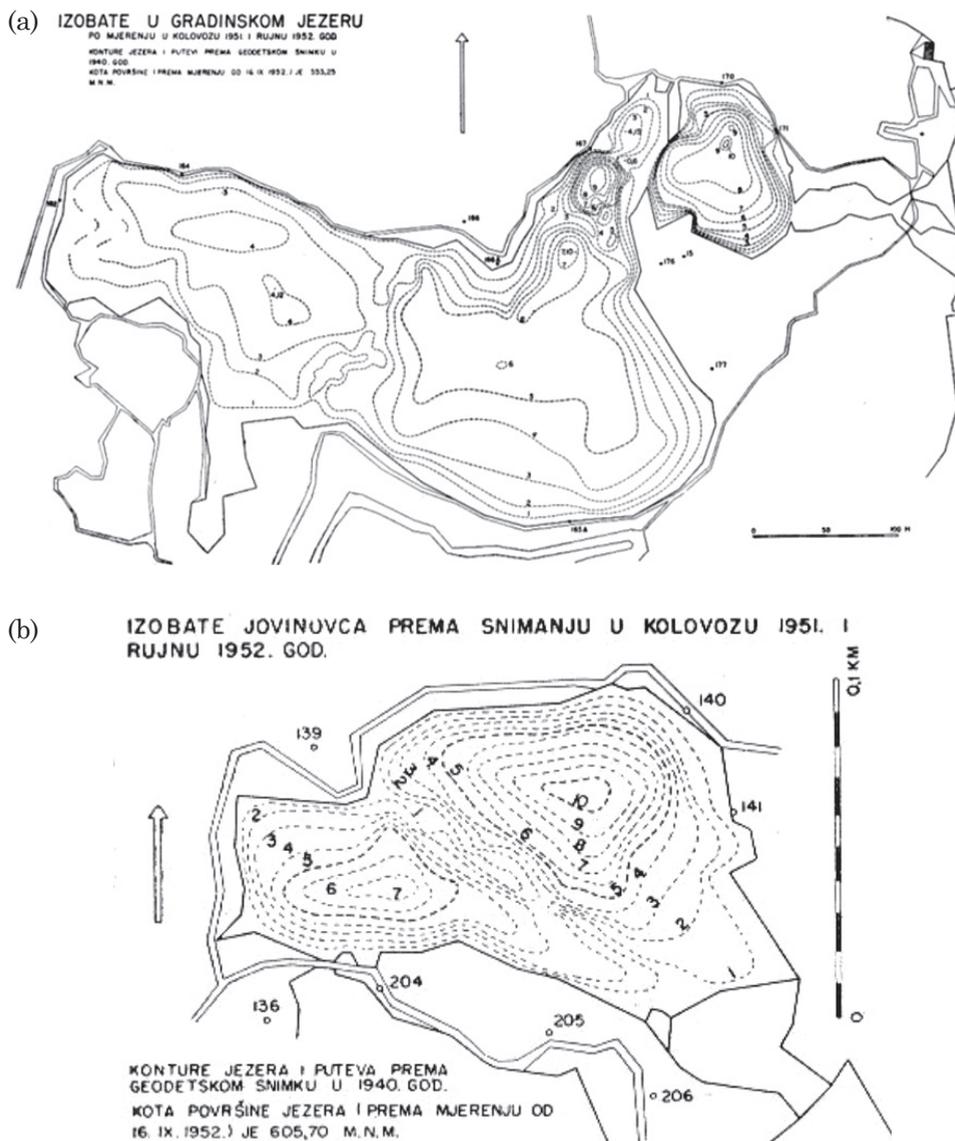


Figure 3. Bathymetry of (a) the Lake 10 and (b) the Lake 6 as given by Petrik (1958). Isobaths are shown for every 1 m. Arrows indicate the direction towards north.

water inflow of the Lake 12 (Kozjak). Petrik noted similar, quick changes for the other lakes as well. These changes were the most prominent at low tufa barriers that both grow and are destroyed quickly. For example, the line of the southern (lower) barrier of the Lake 14 (Gavanovac) completely changed and shifted north-

ward during a period of only 11 years (*i.e.*, from 1940 to 1950). Another example is a small lake described by Gavazzi (1919) as a lake named *Jezerce* with an absolute height of 552.89 m. Only a few decades later, this small lake had merged with the Lake 10 (Gradinsko). Accordingly, Petrik (1958) reported on the single lake (Lake 10, Tab. 1).

Petrik (1958) noted that the lake depths generally increased downstream. In other words, the lakes are the deepest in their downstream areas and shallowest in their upstream regions. The same can be seen from the cross-section of the lake system (Fig. 1) and from the bathymetries of individual lakes (Figs. 2 and 3). Further, the lake floors of small lakes are flatter, while they are more uneven for the older and larger lakes.

More recently, Pribičević et al. (2007, 2010) addressed the bathymetry of the two largest lakes, the Lake 1 (Prošće) and the Lake 12 (Kozjak), while the remaining 14 lakes were not inspected. Although the authors investigated both of the largest lakes, their published results mainly corresponded to the Lake 1. Both studies displayed results obtained from the same measurement dataset. The authors applied an advanced ultrasonic echo sounder measurement technique combined with a Global Position System (GPS). They used two different probes, one emitting high-frequency (210 kHz) signals and the other emitting low-frequency (33 kHz) signals. This dual-frequency technique is based on the different behavior of signals emitted at different frequencies (Fig. 4). The high-

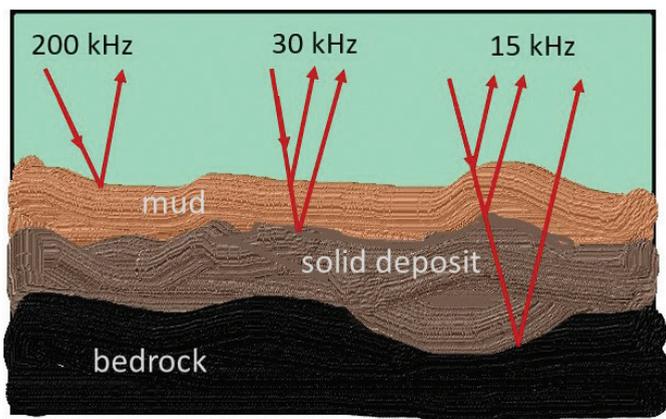


Figure 4. Schematic representation of the signal reflections for different signal frequencies (based on a sketch provided by Pribičević et al., 2007). The signal from the high-frequency probe reflects from the first obstacle (soft or solid), while the low-frequency signal penetrates through softer materials, such as mud, silt, gravel or similar materials. Low frequencies from 7 to 15 Hz penetrate deep in the floor layers, down to the solid bedrock. Therefore, these low-frequency devices are also called sub-bottom profilers. Frequencies between 15 and 30 Hz are used for the detection of boundaries between water and coherent, solid sediments (deposits) or between water and rocks, while high frequencies between 100 and 300 Hz are used for the detection of borders between water and incoherent sediments (mud, silt, etc.).

er frequency reflects off the sediment surface, while the lower frequencies penetrate deeper, and can thus detect different sedimentary structures (*e.g.*, Schrottke et al., 2006).

While analyzing the low-frequency probe data, Pribičević et al. (2007, 2010) noticed two distinguished locations in the northern portion of the Lake 1 with anomalously deep sub-bottom layers (*i.e.*, up to 475 m) laying above the solid bedrock. They also noticed that these depth anomalies coincided with tectonic fault zones. They hypothesized that the anomalies were due to caverns existing below the deposited tufa layers. Although the authors both checked their results and consulted experts in underwater acoustics and geology, they stated that the measurements should be repeated to find an adequate explanation for these anomalies. Finally, the authors concluded that three different portions of the Lake 1 could be distinguished: northern, central and southern. The northern part has anomalously high depths down to the solid bedrock. In this part of the lake, the depth of the tufa deposit varies from 0.42 m to 447.72 m. The central part is characterized by the shallowest layer of deposited tufa, with depths between 0.42 m and 10.24 m. In the southern part of the lake, the depth of the deposited tufa layer is the most uniform, and it varies from 4.52 m to 11.71 m.

3. Meteorology and climatology

Generally, atmospheric processes/conditions are of great importance for lakes since they govern lake stratification and currents (*e.g.*, Boehrer and Schulze, 2008). Additionally, these conditions may directly or indirectly influence the hydrogeochemical and biological processes and conditions in the lake. For example, the input of dissolved matter from the catchment area into the lake depends on the intensity of precipitation; clouds can reduce photosynthesis in a lake, etc. Therefore, climatological and meteorological investigations of the catchment area are essential for solving numerous limnological problems. Scientific investigations of the climate of the PLA are quite scarce. At the end of the 19th century and the beginning of 20th century, which corresponds to the development of natural sciences in Croatia, descriptions of the climate of the PLA were mainly poetic, and they offered few quantitative results. Among them, a monograph by Franić (1910) stands out, where the need for the introduction of meteorological measurements in the PLA has already been recognized. Among others, Franić mentions bora wind with gusts from 50 to 100 km h⁻¹. Further, he states that the mean annual precipitation in the area was approximately 1100 mm, which was less than the average for other Croatian mountainous areas (*e.g.*, 1600 mm for the period of 1875–1890). According to Franić, precipitation was equally distributed over the summer and fall, while fog was rare.

Gavazzi (1919), whose comprehensive study of Plitvice Lakes was actually the first limnological study performed in Croatia, also made short notes on the

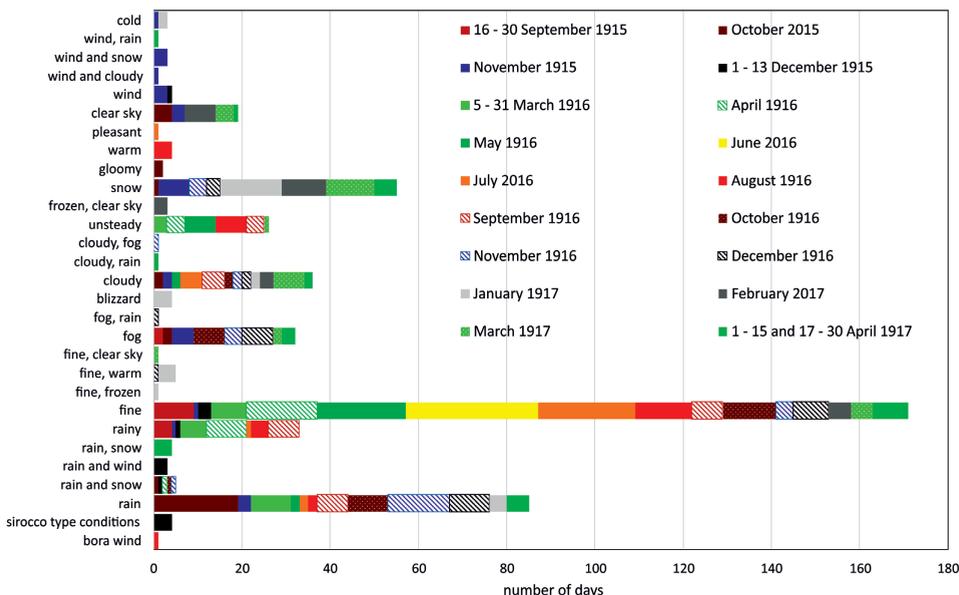


Figure 5. Weather conditions at Plitvice Lakes during 16 September 1915–30 April 1917, according to the notes of Gavazzi (1919).

weather conditions that accompanied his field measurements. Namely, during 16 September 1915–30 April 1917, Gavazzi measured the surface temperature of the Lake 12 (Kozjak) almost every day (for a total of 510 days), and he briefly described the weather conditions that prevailed during a particular measurement. He measured temperature once per day but at different times; thus, the matching notes on the weather conditions correspond to different times of the day. As shown in Fig. 5, Gavazzi most frequently described the weather as fine (*i.e.*, for 178 days, which is about one third of the days). He recorded bora wind only once (6 August 1916), while he observed fog 33 times ($\approx 6.5\%$ of days), which is quite different from information given by Franić (1910). In total, Gavazzi observed rain on 131 days and snow on 67 days, which corresponds to 25.7% and 13.1% of the study days, respectively.

On one occasion, Gavazzi measured the temporal variation in the surface temperature of the Lake 12. Simultaneously, he also measured the air temperature (Fig. 6). However, he did not provide information on the height of the thermometer above the ground.

To date, only Makjanić (1958; 1971–1972) has addressed the climate of the PLA. The author (Makjanić, 1958) highlighted the lack of continuous meteorological observations in the PLA (data time series of PLA were too short). Prior to World War I, only precipitation data were collected at only one measuring site from 1903 to 1910; however, after 1908, these data were untrustworthy. In Au-

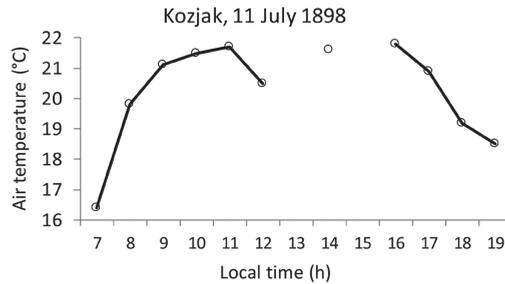


Figure 6. Air temperatures for 11 July 1898 measured next to the Lake 12 (location Kupalište) by Gavazzi (1919). The author did not report on the corresponding measurement height. The minimum air temperature (9.7 °C) occurred on the night between 10 to 11 July, while the maximum temperature (22.9 °C) was observed at approximately 15:30 (local time).

gust 1932, due to the effort of the Geophysical Institute in Zagreb⁵, a weather station was established in Plitvički Ljeskovac. However, until May 1950, the station was more frequently out of operation than in operation due to problems with personnel and the lack of funding and instruments. Finally, in July 1951, the weather station was restored again. Therefore, Makjanić (1958) interpolated missing data based on data collected from other sites, and he acknowledged these shortcomings in his study.

Figures 7 and 8a show the precipitation results, while Fig. 9 shows the annual variations in temperature. For temperature, a complete dataset was

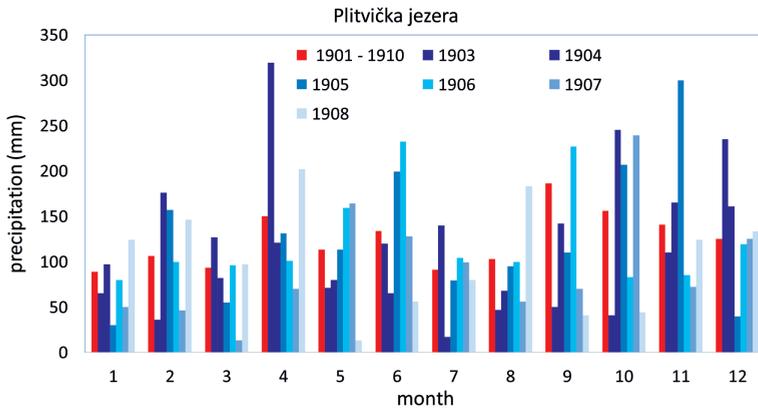


Figure. 7 Annual variations in the amount of precipitation at Plitvice Lakes for the period of 1901–1910 and for some years calculated by Majkanić (1958). Monthly amounts for June and September of 1903, January, November and December of 1905, and, January, February, June, August and December of 1906 are not measured, but were interpolated instead.

⁵ Currently, Department of Geophysics, Faculty of Science, University of Zagreb.

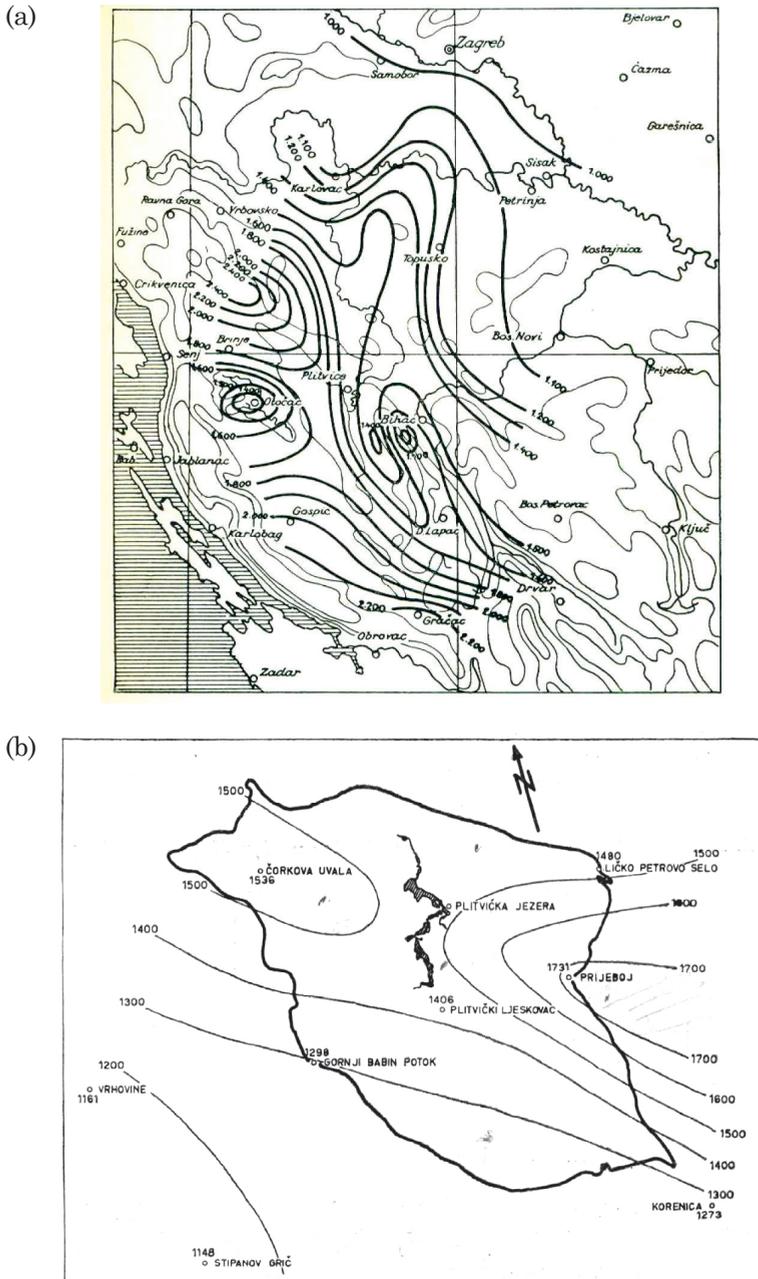


Figure 8. Annual mean precipitation (mm) for (a) the greater area of Plitvice Lakes for the period of 1901–1910, and (b) the Plitvice Lakes Area (PLA) for the period of 1956–1969. Panels a and b are copied from Makjanić (1958) and (1971–1972), respectively.

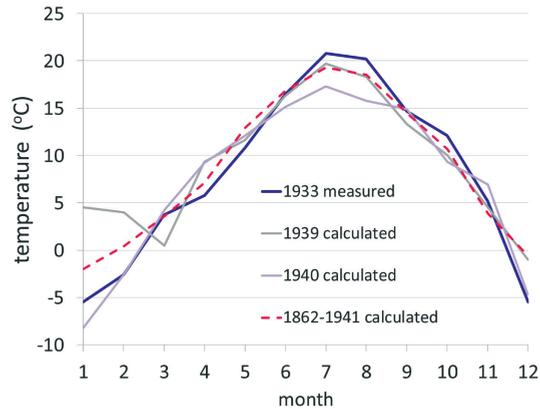


Figure 9. Annual variations in the air temperature at Plitvice Lakes for different periods, as calculated by Makjanić (1958). Temperatures for 1933 correspond to observational data. For 1939, 1940 and 1862–1941 temperatures are calculated from temperatures for Zagreb, Topusko and Gospić (years 1939 and 1940) and Zagreb (period of 1862–1941).

available only for the year 1933. Therefore, Makjanić calculated the annual variations for 1939 and 1940 using temperature data for Zagreb, Gospić and Topusko. Further, based on the long-term measurements of the Zagreb-Grič observatory, he estimated the annual variations in the air temperature for Plitvice Lakes for the period of 1862–1941.

After analyzing the monthly mean air temperatures and the precipitation amounts together with their annual variations patterns, Makjanić (1958) concluded that Plitvice Lakes were positioned between two climatic zones as defined by Köppen climate classification (*e.g.*, Kottek et al., 2006). Namely, some indicators suggest the warm temperate climate C, while others point to the snow climate D. He also remarked that generally, Croatian regions at altitudes above 500 m ASL belong to snow climate zone D. In a later study, Makjanić (1971–1972) corroborated his previous results regarding the climate types found for the PLA. Additionally, he found that the area of transition between the C and D types for the PLA occurred at 700 m ASL. In other words, places within the PLA at altitudes below 700 m ASL belong to the temperate climate zone (C), while places at higher altitudes are in the snow climate zone (D).

In a more recent investigation (Makjanić, 1971–1972), data measured at the PLA were available (Fig. 10 and Tab. 2). Accordingly, Makjanić determined the average spatial distribution of precipitation over the PLA (Fig. 8b) and the annual variations in precipitation, temperature and cloudiness; the seasonal variation in wind directions; various climatic indices (such as the number of days with rain and the number of days with a maximum temperature above 25 °C) and their annual variations. Figures 11–17, which were drawn based on numerical values given by Makjanić, depict these results.

Table 2. List of measuring sites in the PLA in the study by Makjanić (1971–1972).

Measuring site	Site code	Altitude (m)	Data availability
Ličko Petrovo Selo	1	369	1951–1957, 1961–1969
Prijeboj	2	673	1954–1969
Plitvički Ljeskovac	3	650	1952–1969
Gornji Babin Potok	4	740	1961–1969
Vrhovine	5	736	1952, 1954–1969
Korenica	6	658	1948, 1950–1953, 1956–1969
Stipanov Grič	7	1200	1955–1969
Čorkova Uvala	8	837	1954, 1961–1967

Further, Makjanić (1971–1972) analyzed the annual precipitation amounts for Prijeboj, Plitvički Ljeskovac, Vrhovine, Korenica and Stipanov Grič for the period of 1956–1969 (sites 2, 3, 5, 6 and 7, respectively) and he concluded that they were highly variable. He also investigated the duration of snowy winter (Tab. 3) and the maximum depth of snow cover. Not surprisingly, the site with the highest elevation, Stipanov Grič (1200 m ASL, the Site 7 in Tab. 2) was associated with both the highest number of days with snow cover (on average, approximately 108 days per year) and the highest observed snow cover, *e.g.*, 200 cm (28 March 1962). At other measuring sites, the highest observed depths

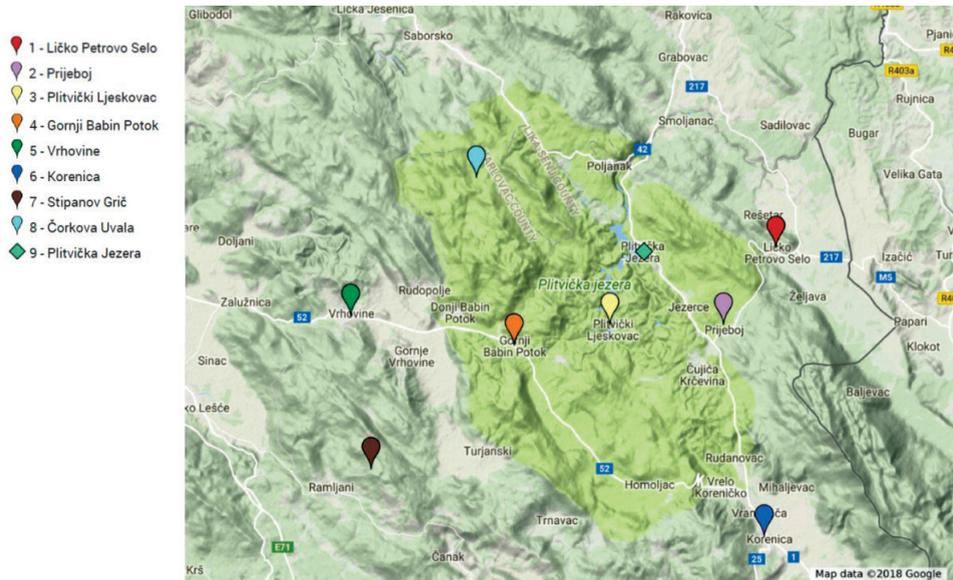


Figure 10. Positions of the eight measuring sites (1–8) in the PLA that were used in the study by Makjanić (1971–1972). Table 2 shows further details. (Source: Google Maps)

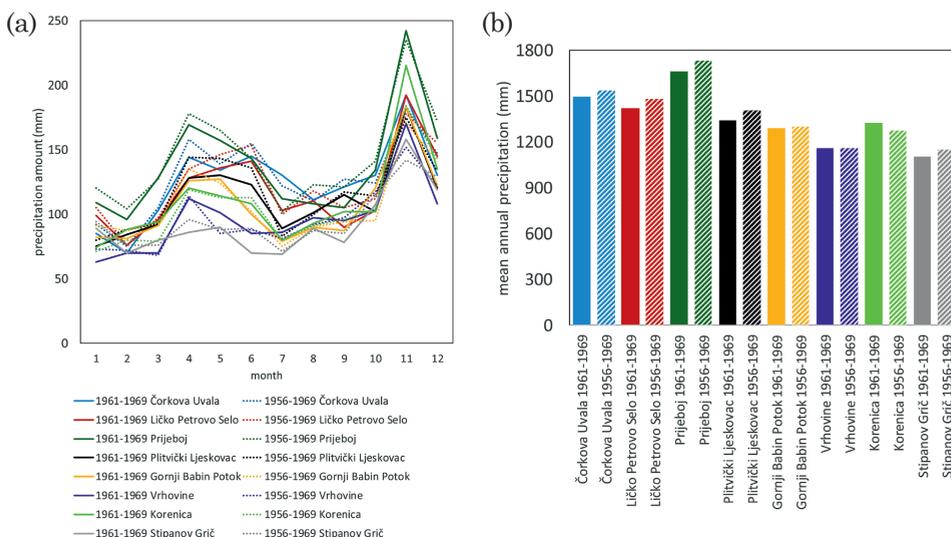


Figure 11. Precipitation characteristics of the PLA: (a) annual variation in precipitation, and (b) mean annual precipitation. Both panels show two periods (calculated by Makjanić, 1971–1972), 1961–1969 and 1956–1969. Measuring sites are given in Fig. 10 and Tab. 2.

of snow cover during the period of 1956–1969 were 149 cm (3 - Plitvički Ljeskovac, 26 March 1962), 141 cm (2 - Prijeboj, 18 February 1969), 140 cm (6 - Korenica, 9 February 1969) and 103 cm (5 - Vrhovine, 13 and 14 February 1963). The author concluded that the snow cover at the PLA melted at least once during the winter. Further, during snowy winters (*i.e.*, the wintertime intervals that start on the first day with snow cover and end on the last day with snow cover), the ground within the PLA is covered with snow approximately half the time. The exact percentages for Plitvički Ljeskovac (Site 3), Korenica (6), Prijeboj (2), Vrhovine (5) and Stipanov Grič (7) were 56, 48, 57, 49 and 58%, respectively.

By analyzing the differences between the amount of precipitation in the warm and cold parts of the year, Makjanić (1971–1972) concluded that both continental and maritime influences were found at the PLA, *i.e.*, the borderline between the maritime (more precipitation in the cold part of the year) and the continental climate regions passes above the PLA. We note that Hunjak (2015), who investigated the spatial distribution of stable isotopes of oxygen and hydrogen in precipitation over Croatia, recently reached a similar conclusion. Namely, precipitation collected at maritime measuring sites generally has a higher share of heavier isotopes in total precipitation than does continental precipitation. Accordingly, the strengthening of the continental influence manifests as a decrease in the share of heavier isotopes in the total precipitation with an increase in the distance from the sea. The results for PLA (No-

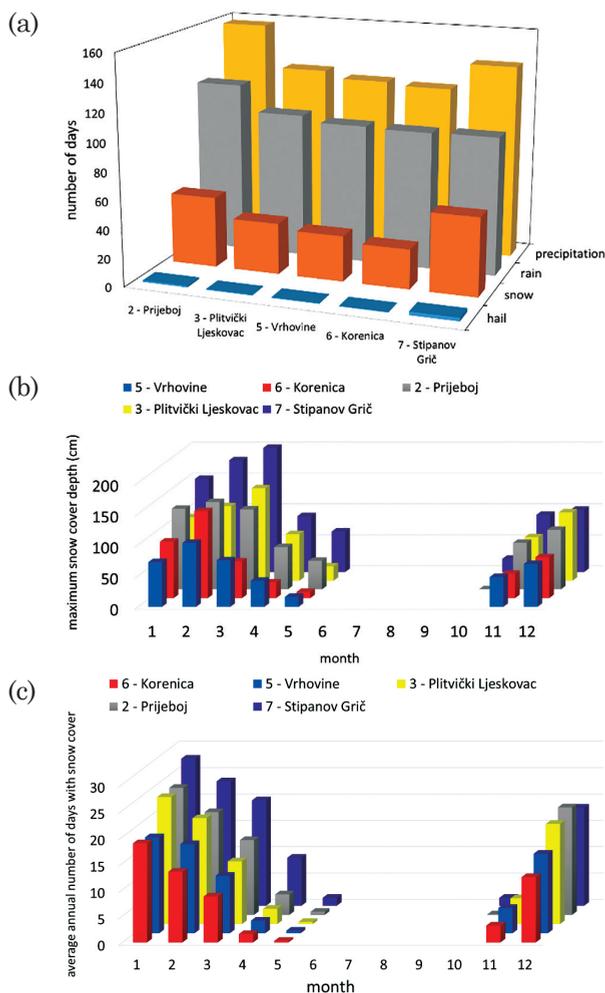


Figure 12. Annual variations in precipitation and snow cover indices for the PLA (calculated by Makjanić, 1971–1972) for 1956–1969: (a) number of days with hail, snow, rain, and precipitation; annual variation in (b) maximum snow cover; and (c) average number of days with the snow cover. Measuring sites are given in Fig. 10 and Tab. 2.

vember 2009–April 2013 data) show a continental influence with respect to the δ -values⁶ for hydrogen (²H) and oxygen (¹⁸O) isotopes, where $\delta^{2}\text{H} = -64.19\text{‰}$

⁶Delta value (‰) is defined as $\delta = 1000 \cdot [R_{\text{sample}} / R_{\text{VSMOW}} - 1]$, where R_{sample} is the ratio of the number of atoms with heavier isotopes and the number of atoms with lighter isotopes within the sample. R_{VSMOW} is the same ratio, but the sample has been standardized according to the VSMOW (Vienna Standard Mean Ocean Water) standard of the International Atomic Energy Agency (e.g., Hunjak, 2015).

Table 3. Duration of snowy winter for the period of 1955–1969 (after Makjanić, 1971–1972). Snowy winter is defined as the winter period, which begins on the first day with snow cover and ends on the last day with snow cover.

Site code	Measuring site	Average duration of the snowy winter (days)	Average snowy winter period	The earliest date with the snow cover	The latest date with the snow cover
2	Prijeboj	148	15 Nov.–12 Apr.	31 Oct. 1966	3 May 1960
3	Plitvički Ljeskovac	137	21 Nov.–7 Apr.	29 Oct. 1955	21 Apr. 1969
5	Vrhovine	138	22 Nov.–9 Apr.	1 Nov. 1955	10 May 1957
6	Korenica	130	28 Nov.–7 Apr.	6 Nov. 1959 and 1961	8 May 1957
7	Stipanov Grič	178	3 Nov.–30 Apr.	7 Oct. 1955	27 May 1957

and $\delta^{2}\text{O} = -9.61\text{‰}$. However, the monthly values of deuterium excess⁷ were for the PLA, in almost all months, $d_{\text{excess}} > 10\text{‰}$, which indicates the influence of Medi-terranean air masses. This maritime signature is seen only in PLA precipitation, while it is not found at other inland measuring sites in Croatia. Another study that also highlighted the continental and maritime influences on the PLA is the dissertation of Babinka (2007). The study focused on the hydrogeology of the PLA, but it showed a relationship between the amount of precipitation and wind directions recorded at a Plitvice Lakes meteorological measuring site during the 2-year period (2003–2004). Approximately 80% of the total 2-year precipitation amount was associated with airflows from the continent (*i.e.*, with N, NE, E, SE and NW winds), while the remaining 20% of the total precipitation corresponded to transports from the Mediterranean Sea (specifically, the S, SW and W flows).

The annual variation in the Köppen's relative temperature (Fig. 14) exhibits an asymmetrical pattern, with fall months that are warmer than their symmetrically positioned spring months. Theoretically, continental influence is accompanied by an annual variation in relative temperature that is symmetrical with respect to July. That is, the months that are equally distant from July (*e.g.*, June and August or May and September) have equal relative temperatures. On the other hand, maritime influence (slower heating in spring and slower cooling in fall) is seen from an asymmetrical pattern, where the fall months are warmer than their spring counterparts. However, fall months may be warmer than spring months due to mountainous influences (snow cover in mountainous areas lasts longer than does snow at low altitudes, and thus, snow cover delays the springtime temperature increase). Therefore, Makjanić (1971–1972) concluded that the asymmetrical shape of the annual variation in the Köppen's relative

⁷Deuterium excess d_{excess} (‰) is defined as $d_{\text{excess}} = \delta^{2}\text{H} - 8\delta^{2}\text{O}$ (*e.g.* Hunjak, 2015).

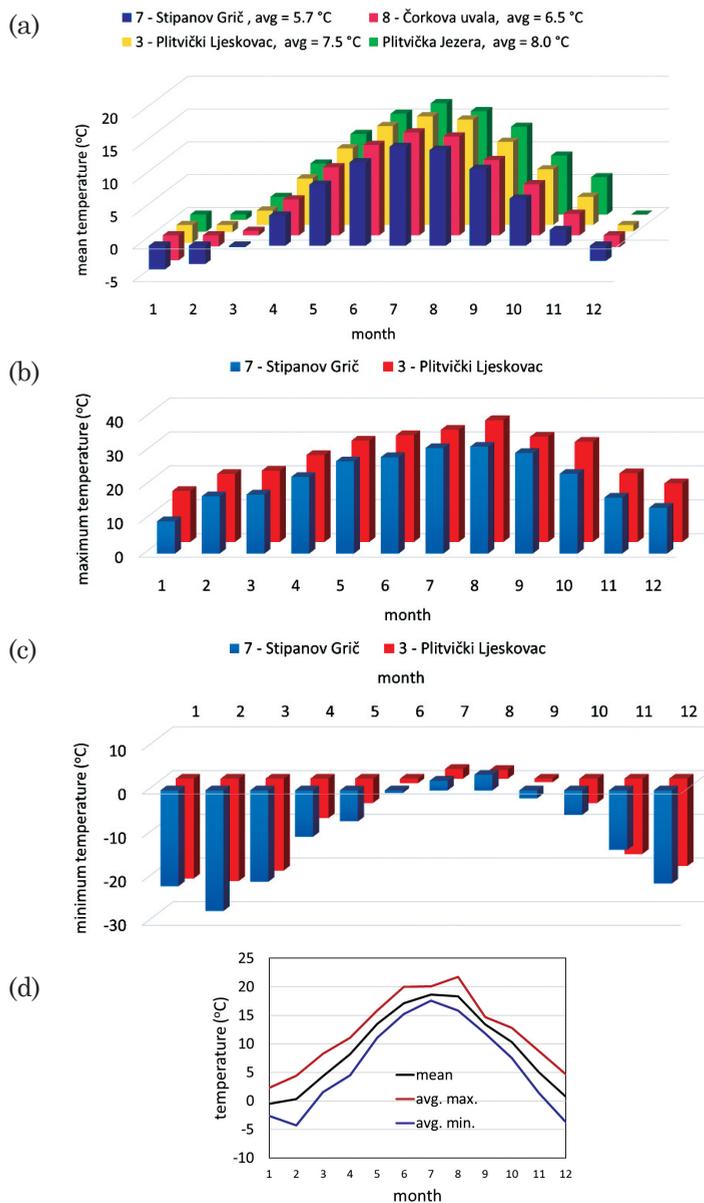


Figure 13. Annual variation in the mean (a), absolute maximum (b), and absolute minimum (c) temperatures for the PLA (calculated by Makjanić, 1971–1972). All data, except for minimum and maximum temperatures for Plitvički Ljeskovac (Site 3), correspond to the period of 1956–1969. The minimum and maximum temperatures for Site 3 are given for the period 1953–1969. The location of the measuring sites is shown in Fig. 10. Panel (d) shows the mean, average maximum and average minimum temperatures for the meteorological site Plitvice (Site 9 in Fig. 10) during the period of 1997–2006 (according to Biondić et al., 2008).

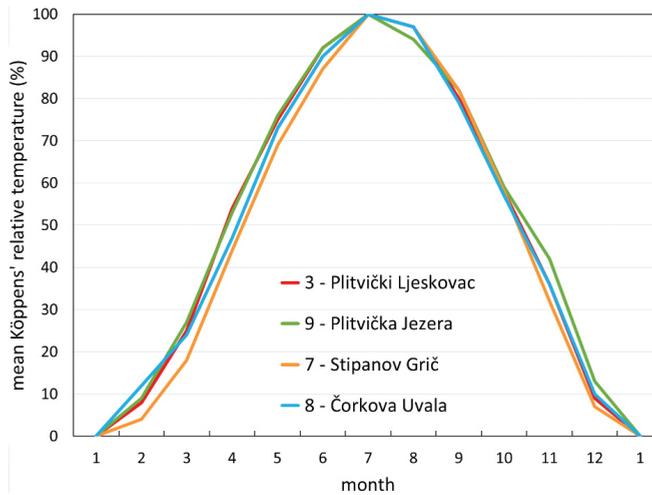


Fig. 14 Annual variation in the Köppen's relative temperature for the PLA during the period of 1956–1969 (calculated by Makjanić, 1971–1972). The relative temperature of the i -th month is $r_i = 100(t_i - t_{\min}) / (t_{\max} - t_{\min})$, where t_i , t_{\min} and t_{\max} are the average temperatures of the i -th, the coldest month and the warmest month, respectively (e.g., Penzar and Makjanić, 1978).

temperature for the PLA was the result of both influences, *i.e.*, maritime and mountainous. However, the author emphasized that the relative contributions of these two influences could not be distinguished.

According to Makjanić (1971–1972), the PLA is the cloudiest area of Croatia (Fig. 16). The sky is the clearest during the summer, *i.e.*, in August (the Site 3) and July (the Site 7), while the cloudiness is maximal in November and December. Based on a comparison of the annual variations in precipitation (Fig. 11a) with the annual variations in cloudiness (Fig. 16c), the author concluded that at the beginning of a year, anticyclonic weather conditions that were accompanied by high amounts of stratiform cloudiness and low precipitation amounts prevailed. During the spring, both the cloudiness and the amount of precipitation are high due to cyclonic activity. In the summer, an etesian regime (e.g., Klaić et al., 2009) is established. This regime is characterized by low cloudiness and low amounts of precipitation. During the fall, cyclonic activity intensifies again, which results in an increase in both the cloudiness and the amount of precipitation. Further, during the wintertime, the sky is somewhat clearer at the Site 7 (Stipanov Grič, 1200 m ASL) than at the Site 3 (Plitvički Ljeskovac, 650 m ASL). This difference is due to the prevalence of low stratiform clouds. Thus, due to its high altitude, the Site 7 is frequently found above the cloud layer. During the summertime, cumuliform clouds prevail. Accordingly, the sky at the sites with lower elevations is less cloudy than is the sky at the mountainous measuring site.

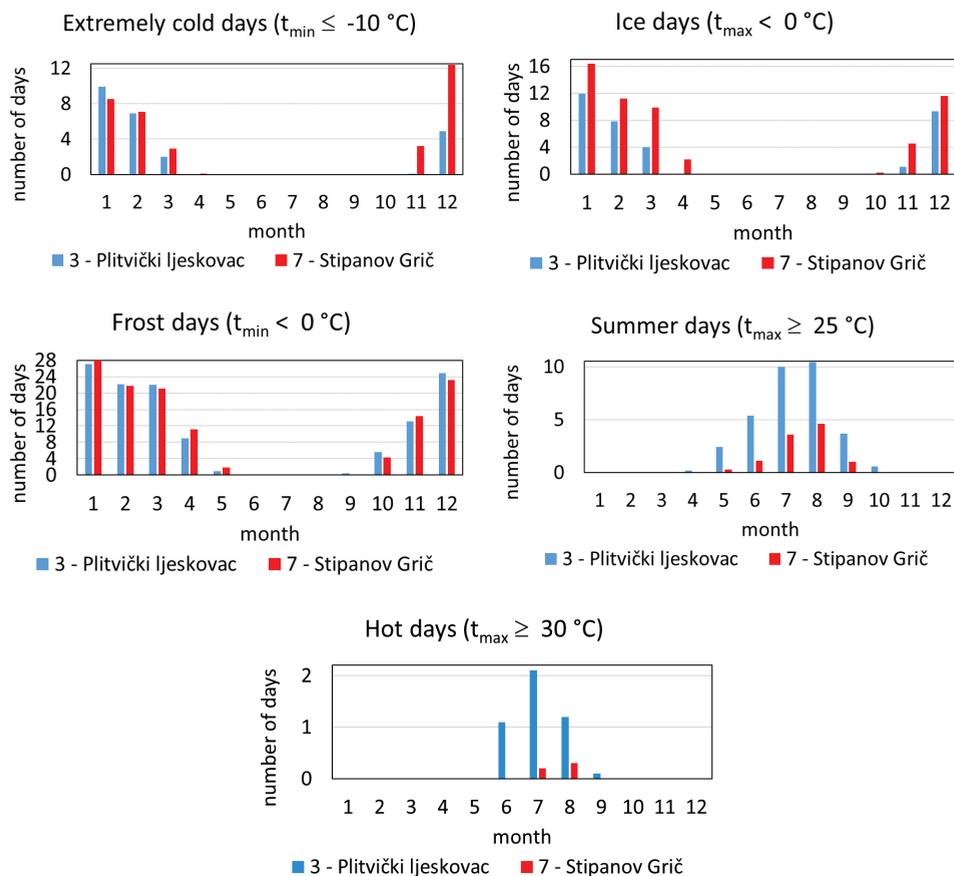


Figure 15. Annual variations in air temperature climatic indices for the PLA for the period of 1956–1969 (calculated by Makjanić, 1971–1972). Ice days are also known as Winter days.

Considering the wind data, Makjanić (1971–1972) analysed only wind directions since the data for wind speed were unreliable. As seen from Fig. 17, at the mountainous Site 7 (Stipanov Grič) northeastern, eastern, southern and southwestern winds prevailed in all four seasons. On the other hand, at the Site 3 with a lower altitude (Plitvički ljeskovac) northern, northeastern and southwestern winds prevailed. We note that northeastern and southwestern flows are prominent at both measuring sites and in all four seasons. Similar shapes of wind roses, stretching in the NE-SW direction with prevailing NE winds, were obtained by Biondić et al. (2008) for the measuring site Plitvice (Site 9 in Fig. 10) of the Meteorological and Hydrological Service of Croatia (hereafter, MHS) for the period of 1998–2003. For individual years, the frequencies of the NE and SW winds ranged from 35 to 45% and 10 to 20%, respectively.

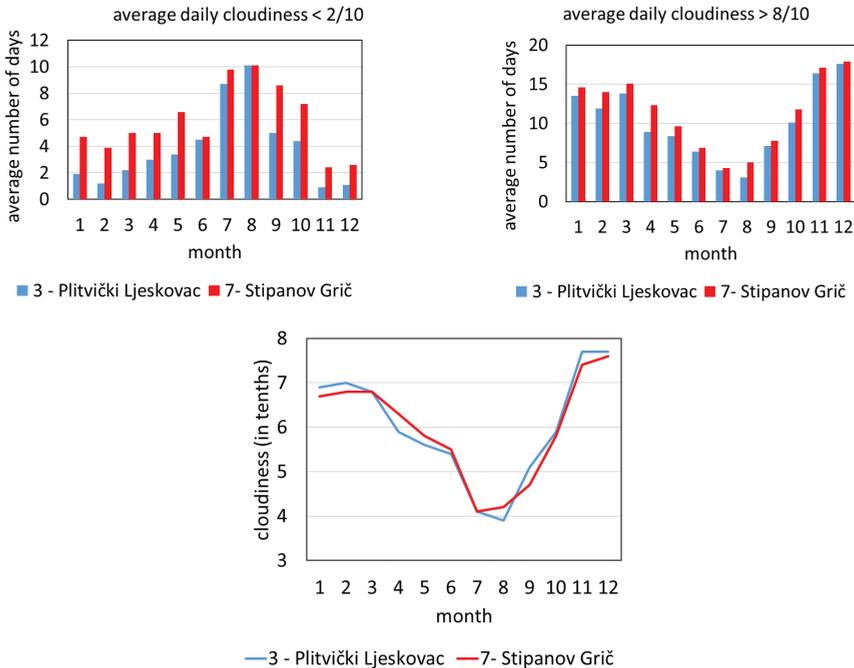


Figure 16. Cloudiness characteristics of the PLA during the period of 1956–1969 (calculated by Makjanić, 1971–1972). Panels (a) and (b) show annual variations in the average number of clear and cloudy days, while panel (c) corresponds to the average cloudiness.

Apart from the old studies of Makjanić (1958, 1971–1972), there are no other investigations that have focused on the climate of the PLA. Additionally, these old studies were based on a time series that were much shorter than 30 years; however, a 30-year time series has been advised as a minimum period length for investigations related to climate analysis (*e.g.*, Zaninović *et al.*, 2008). The Climate Atlas of Croatia (Zaninović *et al.*, 2008) displays the spatial distributions of climatic elements for Croatia and, thus, comprises the results for the PLA. However, the climate conditions between the two nearby places can substantially differ due to different local influences. For example, we noted differences in the amount of precipitation between the sites 1 and 2, which are only 5 km apart (Ličko Petrovo Selo and Prijeboj, Fig. 11). Therefore, due to the spatial resolution of the climate charts, we can only roughly assess the climate of the PLA from the available climate atlas. Similarly, numerous climate studies corresponding to larger spatial scales (*e.g.*, Mikolaskova, 2009) cannot provide fine details of the climatic characteristics of the PLA. Some recent studies, which focused on topics other than climate, such as the hydrogeology and/or hydrogeochemistry of the PLA (*e.g.*, Babinka, 2007; Biondić *et al.*, 2008; Meaški, 2011), provide some climatological information. However, the presented quantitative

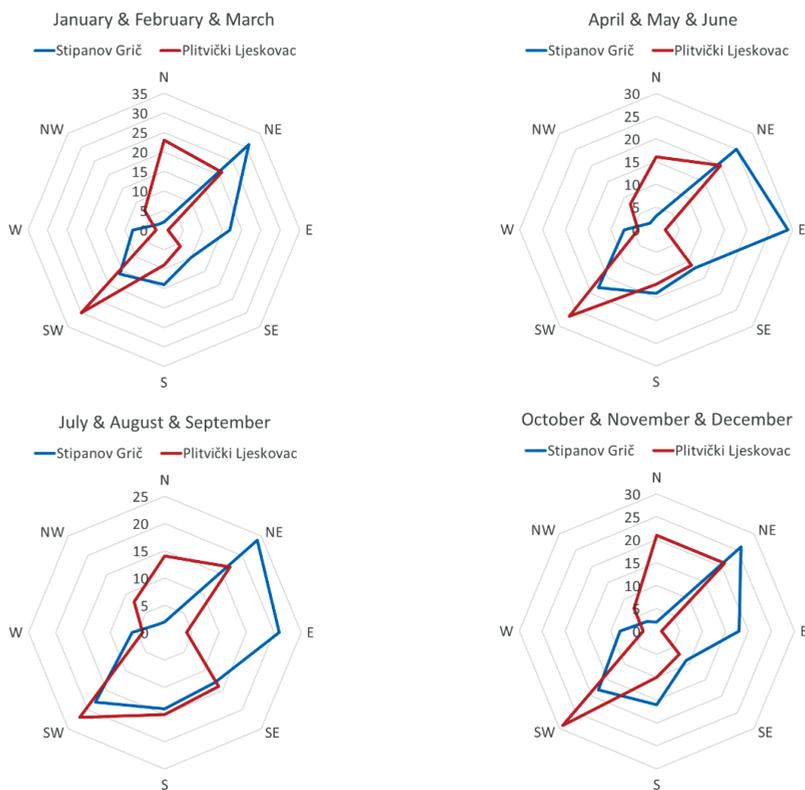


Figure 17. Average seasonal relative frequencies of wind directions for the sites 3 and 7 (Plitvički Ljeskovac and Stipanov Grič, respectively) during the period of 1956–1969 (calculated by Makjanić, 1971–1972).

climatological results correspond to investigation periods that are too short. Figure 13d illustrates one such example.

Finally, some studies have reported on the air and precipitation quality over the PLA (Đuričić, 1986; Bajić and Đuričić, 1995; Špoler Čanić, 2008; Čanić et al., 2009; Herceg Romanić, 2011; Forgić, 2016; Jeričević et al., 2016). Thus, an analysis of 10 years (1981–1982, 1984–1990, and 1997) of daily precipitation samples provided an annual average precipitation of 1478.7 mm, while the average pH value was 4.70. An analysis of precipitation acidity showed that, prior to the year 1990, PLA was affected by acid precipitation due to regional air pollution (Bajić and Đuričić, 1995), and more than 60% of the total precipitation was found to be acidic. After the Croatian War of Independence (1991–1995), the acidity of the precipitation decreased due to the pronounced reduction of Croatian and European emissions of acidifying pollutants. Accordingly, for the year 1997, the average pH at the PLA was 5.30 (Špoler Čanić, 2008). In Croatia, the decrease in the

emissions of pollutants was caused by two factors. The first factor was the decline of industrial activities and energy consumption due to war destruction, while the other factor was the general European trend of reducing the emissions of pollutants to implement legislative regulations regarding pollutant emissions. For the 10 years that were investigated, the average volume-weighted concentrations of ions in the PLA precipitation (in mg l^{-1}) were 2.05 for SO_4^{2-} (as S), 0.88 for NO_3^- (as N), 1.31 for Cl^- , 1.01 for NH_4^+ (as N), 1.99 for Ca^{2+} , 0.48 for Mg^{2+} , 0.67 for K^+ , and 1.32 for Na^+ (Špoler Čanić, 2008, Čanić et al., 2009).

The analysis of hourly airborne particulate matter mass concentrations of particles with aerodynamic diameters of 10 (PM_{10}) and 2.5 μm ($\text{PM}_{2.5}$) observed at the PLA measuring site (latitude 44.9°, longitude 15.6°) during the period of 2011–2014 (Jeričević et al., 2016) provided annual means for PM_{10} between 12 and 17 $\mu\text{g m}^{-3}$. The average ratio of $\text{PM}_{2.5}$ versus PM_{10} concentrations was approximately 0.85. The study also revealed an annual variation in the $\text{PM}_{2.5}/\text{PM}_{10}$ ratio, with a maximum of approximately 0.95 in February and December, and a minimum of approximately 0.61 in August. The daily pattern of particulate matter concentrations exhibited continuous increases in concentrations, starting from the minimum value seen at 6 LST towards the maximum value found at 18 LST. Furthermore, the highest particulate matter concentrations were observed for northeastern winds with speeds between 8 and 10 m s^{-1} . Forgić (2016) analyzed atmospheric ozone (O_3) concentrations observed at Plitvice village during the period of 2012–2013. Considering seasons, concentrations were the highest in spring; in consideration of wind directions, the highest concentrations were associated with northeastern and southwestern flows.

4. Hydrology

Early investigations of the Plitvice Lakes addressed information on the lakes' existence and positions. In a monograph devoted to Plitvice Lakes, Franić (1910) stated that the positions of multiple unnamed lakes were drawn for the first time in the atlas of Martin Stier in 1664, while the term lakes was first time mentioned in the map of Stjepan Glavač in 1673. Lakes divided by barriers were first depicted in the map of *N.N. Jeney* and *N.N. Božić* in 1780, and in the same year, Dominik Vukasović introduced the currently named Plitvice Lakes. Franić also provided numerous hydrological information, such as the data on daily observations of water levels in lakes 1 and 12 (Prošće and Kozjak, respectively) for the year 1908. These observations, which were the first observations of water levels in the PLA, were performed by forestry workers from Plitvički Ljeskovac (the Site 3). According to locals, the year 1908 was extremely dry (drier than any year in the preceding century). However, there were no corresponding measurements in the area that could be used to corroborate this statement. During 1908, the water level varied by 82 and 43 cm for the Lake 1 and the Lake 12, respectively. Franić also reported on the first measurements of water discharge at the outflow

points of the lakes, and he indicated there were water losses across the line from the Lake 12 (Kozjak) to the Lake 15 (Kaluderovac).

The first investigation, that meets scientific standards, is the study by Gavazzi (1919). Although this study was primarily limnological, it provided some interesting hydrological information on the Plitvice Lakes, such as, the lakes altitudes (Tab. 1), and information related to 1908 being an extremely dry year.

Substantial progress in the investigations of the Plitvice Lakes started in 1951, when a multidisciplinary project focused on Plitvice Lakes began (Petrik, 1958, 1961). The project leader was Milivoj Petrik of the Faculty of Civil Engineering, University of Zagreb, and the investigation team was composed of hydrologists, chemists and biologists. Within this project, the hydrological monitoring network was established for the PLA. This network, which has been somewhat upgraded relative to its state in 1951, has operated to the current day. Furthermore, the bathymetric and lake area (Tab. 1), values, which are still in use today, were determined, and submerged barriers were identified. Petrik and his collaborators also studied the lakes' water flows and collected data on the physical, chemical and biological characteristics of the lakes.

For the year 1953, which was rather wet, variations in the lake water levels were sudden and prominent (Tab > 4). For large lakes, seasonal variations in water levels were greater than 50 cm. Furthermore, the highest water levels in major tributaries did not produce the highest water levels in lakes. Thus, the highest water levels in the lakes are caused by long-lasting or heavy precipitation events and snowmelt. However, the lowest water levels in the lakes have always been associated with the lowest water levels of the tributaries. While the maximum water levels in the major tributaries (*i.e.*, *Crna rijeka*, *Bijela rijeka* and *Plitvica*) for 1953 occurred in January, the maximum levels in the large lakes occurred in April. The minimum water levels of the inflowing brooks and the Lake 1 were observed in December, while for *Plitvica* tributary and the Lake 12 these were recorded in October. Petrik also discussed the peculiarity of the Lake 2 (*Ciginovac*), where during the period of 110 days the water level increased 338

Table 4. Water level amplitude and highest 24-hour increase and decrease in water level, respectively, for 1953 (according to Petrik, 1958).

Hydrological station	Maximum water level (cm)	Minimum water level (cm)	Amplitude (cm)	The highest 24-hour increase of water level (cm)	The highest 24-hour drop in water level (cm)
<i>Crna rijeka</i>	95	23	72	15	7
Prošće	66	15	51	12	6
Ciginovac	375	37	338	10	14
Rječica	89	27	62	18	9
Kozjak	80	26	54	8	5
Plitvica	68	18	50	16	12

cm. The author noted that the Lake 2 received an inflow from the Lake 1 only occasionally (*i.e.*, when the water level in the Lake 1 is high enough), while it lost some of its water via subsurface outflow. Additionally, it is possible that some subsurface inflow flows into the Lake 2. Further, the retention capacity of the lakes is high. For the spring of 1953, Petrik estimated a total volume of 400,000 m³ for all lakes, and the volume corresponded to lakes levels that were above drought conditions after intense precipitation and, thus, corresponded to high inflows.

Later, a study by Matoničkin and Pavletić (1967), did not provide much quantitative hydrological information even though it had the word “hydrology” in its title. Apart from some descriptive sections, this paper was entirely focused on the biological component of the lotic ecosystem of Plitvice Lakes. In the mid-1970s, a research project in which the National Park employees participated, began (Dešković *et al.*, 1981, 1984). Within this project, hydrological investigations, including groundwater-tracing experiments, were performed. Based on the results of the tracer experiments, the water divide of the Plitvice Lakes watershed was determined. Biondić (1982) also contributed to the determination of the water divide of the Plitvice Lakes catchment while resolving the different catchments in the Lika region.

In the 1980s, intensive investigations of the water system of Plitvice Lakes were initiated. These studies were performed by the team from the Ruđer Bošković Institute of Zagreb, and they resulted in the determination of the physical and chemical conditions necessary for tufa precipitation from the fresh water and determination of the sedimentation rate and water residence time (*e.g.*, Horvatinčić, 1985; Srdoč *et al.*, 1985), as described in Section 5. Regardless of their hydrogeochemical nature, these studies provided results that are interesting from a hydrological perspective. For example, it was found that the mean residence time of groundwater varied between one and several years, depending on the meteorological conditions, as described in Section 5 (subsection *Mean residence time (MRT)*). Investigations continued after the Croatian War of Independence (*e.g.*, Obelić *et al.*, 2000; Barešić, 2009).

The MHS performed the first detailed hydrological study of the Plitvice Lakes catchment (DHMZ, 1989). This study was based on 5-year time series measurement data. Among others, losses in the system (*i.e.*, differences between the inflow and the outflow discharges) were calculated. Later, Beraković (2005) inspected the lake water balance for the Plitvice Lakes. This investigation indicated there were losses within the catchment, as well as losses in the discharge along the flow from upstream lakes to downstream lakes.

In 2003, a project addressing the post-war anthropogenic pollution of the PLNP and Bihać region in Bosnia and Herzegovina began (ANTHROPOL.PROT, 2006). Sediment analysis revealed that there was no substantial impact of anthropogenic pollution in the area of the PLNP; however, in the Bihać region in Bosnia and Herzegovina, many environmental issues were observed (mainly as a consequence of the war activities during the period of 1992–1995). Among oth-

ers, the ANTHROPOL.PROT project resulted in a thesis by Babinka (2007), which provided a variety of hydrological results. For example, she recalculated the lake volumes (Tab. 1) and developed an improved water balance equation of the lake system:

$$I_{MR+RJ+PL} + I_{pr} + I_u - O_{pump} - O_E - O_u = O_K, \quad (1)$$

where $I_{MR+RJ+PL}$ is the inflow composed of the contribution of the Matica River (MR) downstream of the *Bijela rijeka* and *Crna rijeka* springs and tributaries Rječica River (RJ) and Plitvica Brook (PL). I_{pr} is the precipitation inflow; I_u is the unknown underground inflow; and O_{pump} is the outflow caused by the pumping of water from Lake 12 (Kozjak) for drinking water purposes. O_E is the outflow due to evaporation; O_u is the outflow due to underground water losses from the lakes; and O_K is the outflow due to Korana River, which includes the surface outflow (O_{Ks}) and the water loss from Korana River bed (O_{Ku}).

In comparison with previous calculations of water balance for the Plitvice Lakes system (Beraković, 2005; Zwicker and Rubinić, 2005), Babinka (2007, 2008) considered evaporation from the lake water body, the mixing of lake waters with their tributaries, and the pumping of drinking water from the Lake 12 (Kozjak). She also considered lake stratification (see Section 6). Namely, if the lake is stratified, only the water above the thermocline can evaporate. If the lake is not stratified, all lake water can evaporate. The author found that the groundwater flowing from the Korana River limestone canyon into the karst aquifer plays an important role in the water balance of Plitvice Lakes. Further, in April of 2003 (after the snow had melted), there was no water loss from the riverbed, and the outflow from Plitvice Lakes was $8.48 \cdot 10^6 \text{ m}^3$. However, in September of 2004, approximately $2.42 \cdot 10^6 \text{ m}^3$ of water (which corresponded to 65% of the water coming from the lakes) disappeared into river swallow-holes. Based on isotope hydrology methods (see Section 5), Babinka (2007, 2008) calculated the evaporation from the lakes 1 and 12 and from all other lakes together during two hydrologically different months (Tab. 5a), *i.e.*, one with high spring discharge due to snowmelt and no lake stratification (April of 2003) and the other with low discharge due to dry summer months and established lake stratification (September of 2004). Finally, Babinka assessed that *Crna rijeka* was the most important in terms of feeding the Matica River, and consequently, Lake 1. It contributes to the Matica River by 85%, while *Bijela rijeka* contributes 15%. The most important sources of water for the Lower Lakes (*i.e.*, lakes 13–16) are Plitvica and Sartuk, which through *Veliki slap* waterfall, feed Lower Lakes by 63–84% and 16–37%, respectively. Finally, Babinka highlighted the complexity of the karst lake system, which is still not completely understood. For example, *Crna rijeka* and *Bijela rijeka* are not the only sources feeding Matica. Namely, during the wintertime, approximately $0.72 \text{ m}^3 \text{ s}^{-1}$ of water originates from at least two unknown sources. Additionally, a comparison of the discharge from Plitvice Lakes (including sources and tributaries) and the discharge at the Ko-

rana River (limnograph Luketići) indicated there were possible losses in the Korana riverbed.

In 2005, a collaborative hydrogeological research project by the Faculty of Geotechnical Engineering (University of Zagreb), the Dr. Ivo Pevalek Scientific Research Center of PLNP, and the Institute of Water Research Management (Joanneum Research, Graz, Austria) began (Biondić et al., 2008). The main goal of the project was to improve the knowledge on water genesis and dynamics in Plitvice Lakes. The gained knowledge should serve in future sustainable management (*i.e.*, the sustainable utilization of water) and should help define measures that are appropriate for the protection of surface and groundwater resources. Apart from the project report, this investigation resulted in a paper of Biondić et al. (2010) and the doctoral thesis of Mejaški (2011). In the report, Biondić et al. (2008) provided an overview of the tracing experiments that had been performed to determine the Plitvice Lakes watershed and the pathways of subsurface flows. A tracer, that had been released in the *Crno jezero* ponor (area of Čorkova Uvala), emerged at a point that was 2.3 km away (*i.e.*, Plitvica spring-head) after 48 hours, suggesting there was a low apparent subsurface flow rate of 1.4 cm s^{-1} . The authors argued that these low apparent flow rates were due to the flow through poorly permeable dolomite. This reason also explained why the water quantity at the waterfall *Veliki slap* decreased during the dry summer months. Further, Biondić et al. accentuated that the most important karst springs that feed Plitvice Lakes are *Crna rijeka*, *Bijela rijeka* and Pećina Well in Plitvički Ljeskovac. During the dry periods, these three sources provide an inflow to the lake system of approximately $0.5 \text{ m}^3 \text{ s}^{-1}$, while during the rainy periods the inflow is several times higher, especially due to the contribution *Crna rijeka*. For the Lake 12 (Kozjak), an important water inflow (approximately $0.5 \text{ m}^3 \text{ s}^{-1}$), is provided by the Rječica River (which receives water from several small seepage springs and waterways draining from the large area of low permeability dolomite). Another significant source of water is the Plitvica Brook, which seeps down over the 78 m high *Veliki slap* waterfall into the Korana River. This spring has rather strong karst well (Plitvica Well), with an outflow of at least $0.27 \text{ m}^3 \text{ s}^{-1}$.

Apart from the inventory of water sources, using the identification of subsurface water pathways and the porosity/permeability of underlying rocks, Biondić et al. (2008) evaluated the water balance of the lakes based on the following equation:

$$\Delta V = P + I_{Sg} + I_{Sug} - O_s - E - Q = 0, \quad (2)$$

where P is precipitation amount; I_{Sg} is the channelized gauged river inflow; I_{Sug} is the channelized and non-channelized unmeasured inflow; O_s is the outflow; E is the evaporation; and Q is the pumping capacity of water for the water supply. The authors argued that, though water flows through the lake system, it is retained in the system for a relatively short time. This result was confirmed by

measurements, which showed that both the individual lakes and the entire system reacted quickly to an increase or decrease of inflow. Further, multiyear observations showed that volume changes were negligible during stationary conditions. In other words, the inflow to lakes is equal to the outflow (Eq. 2). Table 5b shows the mean water balance components determined based on multiyear observational data, where the area of the direct watershed is approximately 2 km².

Table 5. a) Monthly evaporation from Plitvice Lakes for two different spring discharges and lake stratification setups: 1) high discharge due to snowmelt and no lake stratification (April 2003) and 2) low discharge due to dry summer months and established lakes stratification (September 2004), as calculated by Babinka (2007, 2008) based on isotope-hydrology methods.

Lake code	Lake	Monthly evaporation (mm)	
		High discharge and no lake stratification	Low discharge and stratified lake
1	Prošće	9.0	14.5
12	Kozjak	12.3	16.0
	All other lakes	4.6	8.9
	Total	25.9	39.4

Table 5. b) Annual mean water balance components of Eq. 2 for Plitvice Lakes system as assessed by Biondić et al. (2008) based on multiyear observations. The area of the direct watershed is approximately 2 km².

Component	Flux rate (m ³ s ⁻¹)	% of inflow/outflow
I n f l o w		
P –precipitation	0.10	3
I_{Sg} –gauged stream inflows	2.61	90
Sušanj	0.06	2
Matica	2.14	74
Rječica	0.41	
I_{Sug} –channelized and non-channelized unmeasured inflows (estimated from Eq. 2 as a difference between $O_s + E + Q$ and $P + I_{Sg}$)	0.20	7
O u t f l o w		
O_s –outflow from Lake 12	2.81	97
E –evaporation	0.03	1
Q –pumping of water from Lake 12	0.06	2

Based on the available hydrogeological data (specifically, the lithostratigraphic characteristics of rocks, geologic structure, subsurface flow tracing experimental data, hydrochemical and isotopic water analyses and hydrologic characteristics, such as spring and stream discharges) Meaški (2011) and Meaški et al. (2016a) delineated the main Plitvice Lakes sub-catchments (namely, Ma-

tica, Plitvica and Jezera sub-catchments) into smaller hydrogeological units (Fig. 18). However, the author states that due to the limited availability of hydrogeological data, the presented water divides of the smaller hydrogeological units should be considered as preliminary (Meaški, 2011).

The sub-catchment Matica is composed of the hydrogeological units of *Crna rijeka*, *Bijela rijeka* and Ljeskovac springs (Fig. 18). It encompasses 83.7 km² (*i.e.*, approximately 55% of the total area of the Plitvice Lakes catchment), and it contributes to approximately 2/3 of the total water inflow into the lakes system. The sub-catchment Plitvica (40.5 km², *i.e.*, approximately 27% of the total catchment area) consists of three hydrogeological units—Sartuk, Plitvica spring (west-

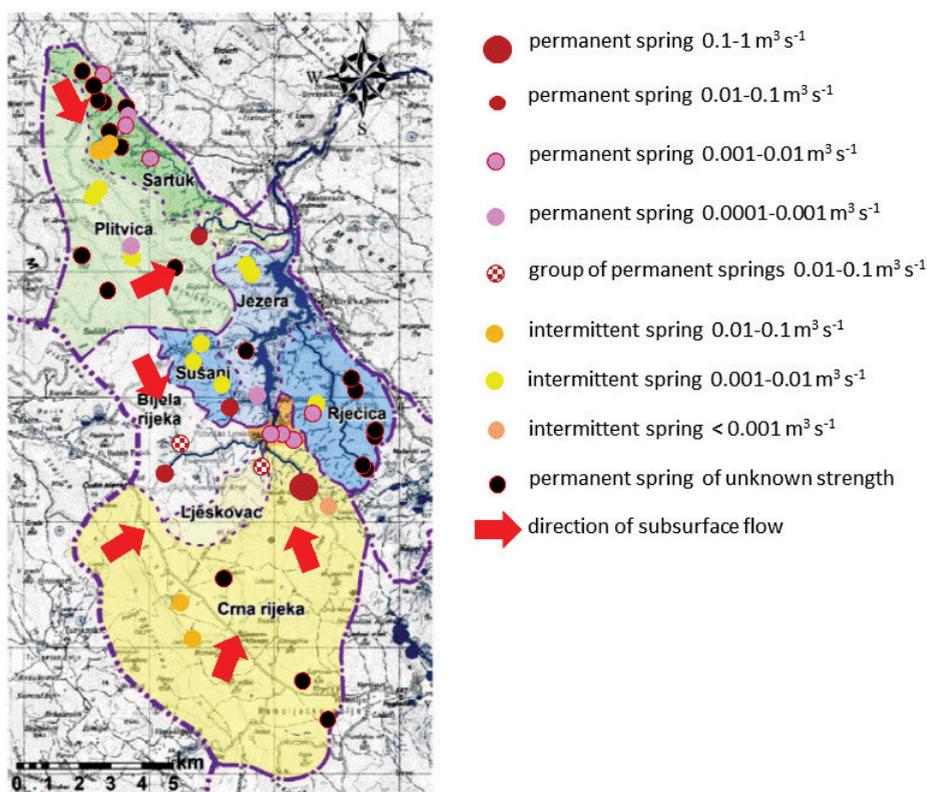


Figure 18. Composite display of the Plitvice Lakes catchment based on the results of Meaški (2011). It shows the delineation of the Plitvice Lakes catchment into three main sub-catchments (Matica, Plitvica and Jezera). Based on hydrogeological data, the main sub-catchments are divided into smaller hydrogeological units (each unit is represented by a different color). Further, it displays the positions of permanent and intermittent springs and the directions of subsurface flows. Violet lines represent the following: the thick dash-dotted line is the water divide line of the Plitvice Lakes catchment, the long-dashed lines are water divides between the main sub-catchments, and the short-dashed lines are borders of the smaller hydrogeological units within each main sub-catchments.

ern, larger light green area in Fig. 18) and Plitvica watercourse (eastern, smaller light green area). Finally, the sub-catchment Jezera (27.5 km², *i.e.*, approximately 18% of the catchment area) contributes approximately 1/3 of the total inflow of water to the lakes system. Meaški (2011) determined the water balance for each sub-catchment, and he compared the mean discharges calculated for the 1960–1990 period with the mean discharges observed during the 1981–2008 period (Tab. 6). The author calculated the water balance for the hydrogeological units shown in Fig. 18 (not shown here) and, afterwards, for the three main sub-catchments (Tab. 6). In the evapotranspiration calculation, Meaški employed two approaches—Turc’s (Eq. 3) and Coutagne’s (Eq. 4), respectively:

$$ET_T = P / [0.9 + (P/L)^2]^{1/2}, \quad (3a)$$

where ET_T is the mean annual Turc’s evapotranspiration (mm), P is the mean annual observed precipitation (mm), L is the quantity that is calculated from the annual mean temperature t (°C) as

$$L = 300 + 25 \cdot t + 0.05 \cdot t^3. \quad (3b)$$

If the monthly mean precipitation amount (P_i , where $i = 1, \dots, 12$) and the monthly mean temperatures (t_i) are available, then, the annual mean temperature t in Eq. 3b is replaced by $\Sigma(P_i \cdot t_i) / \Sigma P_i$ (Turc, 1954). Coutagne’s mean annual evapotranspiration ET_c was determined from:

$$ET_c = 0.2 + 0.035 \cdot t, \quad (4)$$

where the condition condition $P \geq 0.5 \cdot (0.8 + 0.14 \cdot t)$ must be fulfilled. Over the PLA, Eq. 3 produced somewhat higher values of the mean annual evapotranspiration (420–540 mm) than did Eq. 4 (400–520 mm). Further, Meaški calculated the annual effective precipitation (P_e) from the annual mean measured precipitation P :

$$P_e = 0.83 \cdot P - 250. \quad (5)$$

Furthermore, he determined the evaporation from free water surfaces (E) as:

$$E = 11.25 \cdot e_0 \cdot (1-R) \cdot (1 + 0.225 \cdot v), \quad (6)$$

where E is given in mm per month, e_0 is the monthly mean saturation pressure of water vapor (hPa), R is the monthly mean relative humidity (%), and v is the monthly mean wind speed (m s⁻¹). Figure 19 shows the annual variation in evaporation calculated from meteorological data that had been measured in the vicinity of Lake 12 during the 1995–2007 period.

Table 6. Annual mean water balance for three main Plitvice Lake sub-catchments (see Fig. 18) for the period of 1960–1990 (Meaški, 2011). A is the area, P is the average annual precipitation, P_e is the effective annual precipitation, ET is the annual evapotranspiration, P_e/P is the runoff coefficient, $Q_{calc} = A \times P_e$ is the calculated annual mean discharge, and Q_{obs} is the mean observed discharge, which corresponds to the period of 1981–2008.

Sub-catchment	A (km ²)	P (mm)	P_e (mm)	ET	P_e/P	Q_{calc} (m ³ s ⁻¹)	Q_{obs} (m ³ s ⁻¹)
Matica	83.7	1247	788	459	0.63	2.087	1.812
Plitvica	40.5	1450	966	484	0.67	0.885	0.655 (Plitvica Bridge)
Jezerca	27.5	1363	886	477	0.65	2.746	2.450 (Kozjak Bridge)

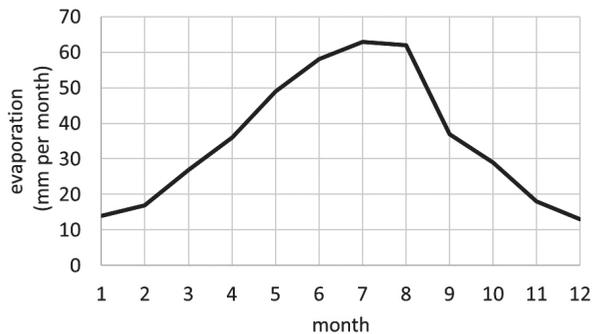


Figure 19. Annual variation in monthly evaporation from free water surface (E , mm per month) calculated by Meaški (2011) from Eq. 6. Meteorological data employed in the calculation had been measured at a site near Lake 12 (Site 9 in Fig. 10) during the period of 1995–2007.

Other recent hydrological studies of the PLA have addressed trends in the water levels and discharges and their association with the growth of tufa barriers and water losses from the lakes system (Zwicker and Rubinić, 2005; Rubinić et al., 2006, 2008; Lončarević Gliha, 2012; Bonacci, 2013a, 2013b). Thus, based on data collected during the 1952–1990 period, Zwicker and Rubinić (2005) reported upward trends in both the annual minimum and the annual average water levels at Lake 1 and Lake 12 (Prošće and Kozjak, respectively). The authors also give the following relationships:

Lake 1

$$\text{The annual average water level} = 1.1207 \cdot \text{Year} - 2154.3, \quad (7a)$$

$$\text{The annual minimum water level} = 1.3995 \cdot \text{Year} - 2719.9, \quad (7b)$$

Lake 12

$$\text{The annual average water level} = 0.2959 \cdot \text{Year} - 532.27, \quad (7c)$$

$$\text{The annual minimum water level} = 0.5158 \cdot \text{Year} - 982.71, \quad (7d)$$

where all water levels in Eqs. 7a–7d are given as departures from the zero water level (cm). Further, upward trends in the water level were accompanied with downward trends in the discharges (downward trends were also observed over the entire Dinaric karst). For the entire lake system, Zwicker and Rubinić estimated a decrease in the annual average and minimum discharges by $0.041 \text{ m}^3 \text{ s}^{-1}$ per year (*i.e.*, by 1.15%) and $0.0042 \text{ m}^3 \text{ s}^{-1}$ per year (*i.e.*, by 0.4%), respectively. Specifically, for the Lake 12, for which measured discharge data were available, the annual average discharge during the investigated 39 years decreased by $0.165 \text{ m}^3 \text{ s}^{-1}$ per year. Furthermore, based on the combination of observed water level and discharge data for the Lake 12 with the stage-discharge curve, Zwicker and Rubinić estimated that during 1952–1990, tufa in Lake 12 had been growing on an average of 0.56 cm per year. On the other hand, the growth of tufa in Lake 1 was approximately three times faster, *i.e.*, 1.5 cm per year. The latter result well agrees with the result of Srdoč et al. (1985), who found a value of 1.35 cm per year for the Lake 1. According to Srdoč et al., this value has been valid since the mid-13th century.

Apart from confirming the previous results of Zwicker and Rubinić (2005), Rubinić et al. (2008) reported on the PLA hydrological network and its restoration after the Croatian War of Independence (Tab. 7); the authors also discussed the water losses in the lake system and provided trends in the annual mean and minimum discharges for the Kozjak Bridge and Luketići measuring sites for the period of 1952–2003:

$$\begin{aligned} \text{Kozjak Bridge} \quad \text{The annual average water discharge} = \\ = 0.0305 \cdot \text{Year} + 63.663, \end{aligned} \quad (8a)$$

$$\begin{aligned} \text{Luketići} \quad \text{The annual average water discharge} = \\ = 0.041 \cdot \text{Year} + 84.392, \end{aligned} \quad (8b)$$

where discharge is given in $\text{m}^3 \text{ s}^{-1}$. The authors noted that the upper portion of the Korana River exhibited more pronounced water losses than Lake 12. Furthermore, water losses observed at the upper part of the Korana River during 1961–1990 were the highest relative to the losses that were concurrently found in other parts of the karst region of Croatia. Finally, the authors noted that the intensity of tufa barrier growth was different for different lakes in the PLA and also varied in time.

Biondić et al. (2010, 2016) and Meaški et al. (2016) also addressed water losses. Biondić et al. (2016) investigated losses at the upper part of the Korana River. Based on hydrogeological investigations, they found that during the dry periods in the sinking zone of the Korana River, the groundwater level within the active aquifer was approximately 25 m below the riverbed. Therefore, a relocation of the current water-supply capture would be desirable. Further, tracing tests confirmed the results of Babinka (2007), who showed that the Plitvice Lakes catchment is connected to the Una River (Bosnia and Herzegovina) catchment,

which implies there is a transboundary character of the aquifer. Furthermore, Biondić et al. (2010) and Meaški et al. (2016) assessed the *Veliki slap* waterfall, which has exhibited large water losses during dry periods of the last *ca.* 20 years. They found that tufa formation occurs in Plitvica Brook. At some locations of the Plitvica watercourse, tufa barrier growth is so intense that it elevates the riverbed and, consequently, causes the overflow of water into nearby karst meadows, which have sinkholes. Thus, during dry periods, a large amount of Plitvica Brook water is lost due to these sinkholes. Biondić et al. (2010) noted that in the past, the losses were lower since the local inhabitants cleaned and cut troughs in the tufa barriers; thus, they protected the meadows from flooding. In recent decades, inhabitants have been more oriented towards tourism, while activities associated with cattle breeding (maintenance of pastures) are fading.

Table 7. Periods of hydrological measurement within the PLA (according to Rubinić et al., 2008). All instruments operated from the starting year until 1990 and afterwards as of the year of restoration.

Site	Watercourse	Gauge starting year	Limnograph starting year	Restored
Plitvički Ljeskovac	Bijela rijeka	1979	1981	1995
Plitvički Ljeskovac	Crna rijeka	1979	1981	1996
Plitvički Ljeskovac	Matica	1951	1979	1995
Prošće	Lake 1	1951	1981	1995
Plitvička Jezera	Rječica	1979	1979	2002
Kozjak Bridge	Lake 12	1978	1978	1995
Rodić Poljana	Sartuk	1979	1981	2001
Plitvice	Plitvica	1951	1979	1996
Luketići	Korana	1977	1977	1995
Plitvički Ljeskovac	Sušanj	1979	1990	–
Plitvički Ljeskovac	Kavgga	1979	–	–
Plitvički Ljeskovac	Pećina	1979	–	–

Bonacci (2013a) analyzed time series of the annual mean and minimum and maximum water levels for the lakes 1 and 12 for two periods for which data were available (pre-war and post-war, respectively). He concluded that the minimum, average and maximum water levels at the Lake 12 continuously increased during the first period (1953–1990), while during the second period (2001–2011), they decreased. According to the author, the latter resulted in an alarming downward trend in discharges from the Lake 12 in the post-war period. However, a later revision of these results (Bonacci, 2013b) revealed that the downward trends were not alarming; rather, they were ostensible since the entire time series (1953–2011, with a multiyear interruption during the war) was not homogenous. Namely, the positions of the zero water level points in the two periods (pre- and post-war) differed. After the data were corrected, an uniform upward trend in all three annual water levels (minimum, average and maximum) was

found. The upward trends in water levels that were found for both the Lake 1 and the Lake 12 (Prošće and Kozjak, respectively) were the most likely caused by the natural growth of tufa barriers (Bonacci, 2013a).

5. Geochemistry of waters, tufa barriers, lake sediments and soils

The first geochemical investigations of the PLA were performed within geographical, hydrological and limnological studies. During the last 100 years, the most frequent investigations included measurements of lake temperatures (see Section 6), which is an important factor that affects the ecosystem and tufa growth. Gavazzi (1919) reported on chemical analyses of the lakes 1, 12 and 13 (Prošće, Kozjak and Milanovac, respectively) waters and on the water hardness of the various lakes. In lake water, he found calcium oxide (CaO), magnesium oxide (MgO), silicon dioxide (SiO₂), total iron(III) oxide plus aluminum(III) oxide and phosphorus pentoxide (that is, Fe₂O₃ + Al₂O₃ + P₂O₅), sulfur trioxide (SO₃), and oxygen (O) available for oxidation. However, the author did not report details of the applied analyses methods, nor did the author report the units that corresponded to the presented results. On several occasions, Gavazzi determined the water hardness⁸ of the lakes by applying Clark's soap method⁹. Based on the results for CaO and MgO, he found higher hardness during wintertime than in summertime. The author argued that during the summertime (*i.e.*, during the period of vegetation), aquatic plants use carbon from carbonic acid, which decalcifies the lake water. Further, based on an experiment performed at Lake 12, Gavazzi concluded that the water hardness was lower at the lake surface than at its bottom, which he again attributed to more intense decalcification at the lake surface relative to its bottom portion.

Gavazzi (1919) also analyzed mud samples collected at Lake 12. He noted that offshore (≈ 10 m), there was always at least some mud sediment at the lake bottom, *i.e.*, the lake bottom was not completely incrustated by tufa, as it had been believed up to that time. The sediment was composed of fine white-yellowish particles, and it was mainly calcareous, having approximately 89.33% and 2.12% of CaCO₃ and MgCO₃, respectively. He also reported on chemical compounds containing iron and phosphorus. In addition, Gavazzi engaged a botanist (Ivo Pevalek) to perform supplementary analyses of mud samples. Thus, it was revealed that the mud contained an abundant amount of diatom¹⁰ debris. How-

⁸ Water hardness is a measure of the quantity of divalent ions (*i.e.*, divalent salts) in the water. The most common sources of water hardness are calcium and magnesium salts.

⁹ Thomas Clark published the soap method in 1847 in *Chemical Gazette* (Collins, 1928; Green, 1957). Description of this method can be found in Collins (1928).

¹⁰ Diatoms are a major group of algae and are among the most common types of phytoplankton. (Phytoplankton are photosynthesizing microscopic organisms that inhabit the open water of the upper sunlit layer oceans, lakes and large rivers.)

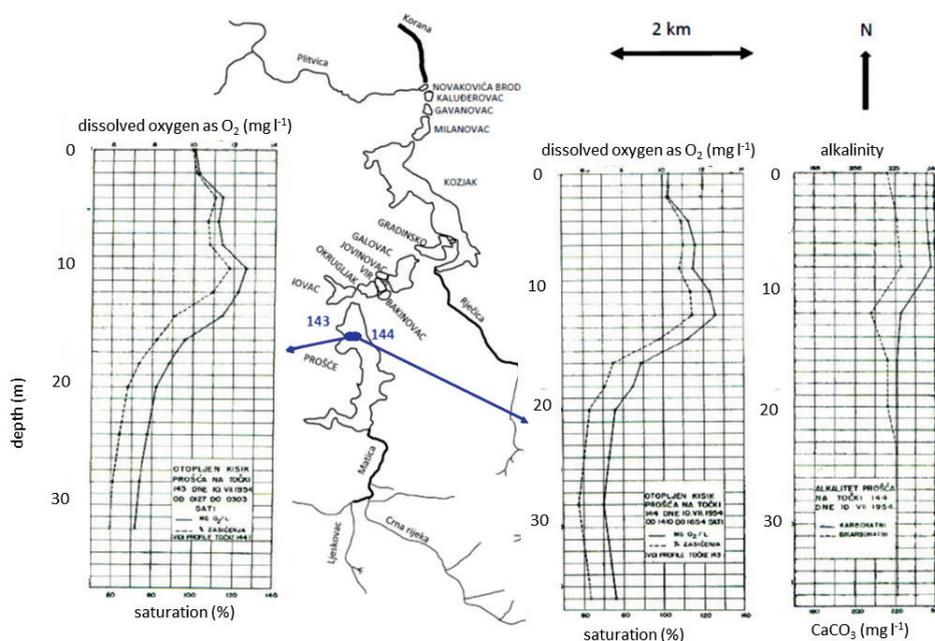


Figure 20. Vertical profiles of dissolved oxygen and alkalinity for two points in Lake 1 on 10 July 1954 (profiles taken from Petrik, 1958). The positions of the measurements points within the lake system are shown by blue circles (measurement points 143 and 144). For dissolved oxygen (left and middle profiles), full lines show the observed values (mg l^{-1}), while dotted lines are the levels of saturation (%). For alkalinity (right profile), full and dotted lines correspond to carbonate and hydrogencarbonate alkalinity, respectively. Double arrow thick lines correspond to the 2 km distance that is shown to demonstrate the size of the lake system and its tributaries. North is indicated by the thick black arrow.

ever, the debris was so small that, at that time, the available equipment enabled the recognition of only 1–2% of the clear shapes, where mainly *Cyclotella* with a diameter of 19–24 μm , was identified¹¹.

Petrik (1958, 1961) addressed to the dissolved oxygen (hereafter, DO), water alkalinity¹², and water hardness in the Plitvice Lakes. One such example is depicted in Fig. 20. Based on numerous measurements, he concluded that brooks provided approximately 10 mg of DO per liter. Additional sources of DO were atmospheric oxygen that is dissolved in lakes water and photosynthesis, which occurs within lakes during daylight hours (on the other hand, the consumption of oxygen due to respiration and decomposition occurs over all 24 hours). Thus,

¹¹ Gavazzi (1919) remarked that almost certainly one of *Cyclotella* found was *Cyclotella operculata* var. *radiosa* Grunow.

¹² Alkalinity is a measure of a sample (in the present context, of lake water) to neutralize acid. It is expressed in mg l^{-1} of calcium carbonate (CaCO_3) or bicarbonate anion HCO_3^- .

in general, high levels of saturation or even oversaturation are rather common for the Plitvice Lakes, even in the deeper layers of the lakes. Further, Petrik noted that the vertical profile of DO roughly followed the vertical profile of temperature (see Section 6). In other words, the more prominent thermal stratification was associated with the more pronounced stratification of DO. Thus, for the isothermal vertical profile of temperature, the concentration of DO was approximately constant with depth. On the other hand, if the vertical distribution of DO is uneven (*i.e.*, lake is stratified), the DO concentration in the epilimnion is close to saturation, the metalimnion (thermocline) is oversaturated (oversaturation can be as high as 140%), and the level of saturation in the hypolimnion is within the range of 50–90%, which corresponds to concentrations between 7 and 12 mg l⁻¹. Additionally, during the summertime, the Plitvice Lakes are oligotrophic¹³. Oligotrophy is particularly pronounced downstream of the submerged barrier in Lake 12 (Petrik, 1958), while Lake 1 is the most likely to be mesotrophic (Petrik, 1961).

Tufa deposition

Petrik (1958) also discussed tufa barriers growth. Apart from the example of the merging of small lake *Jezerce* with Lake 10 (Gradinsko) due to the quick growth of barriers (see Section 2), he described a widening of barriers and their downstream propagation. He pointed to the results of Pevalek (1935, 1938) regarding the importance of several plant species, from which and around whose remains tufa is formed. A moss, *Cratoneuron commutatum* builds the vertical face of a barrier, while *Bryum pseudotriquetrum* (also a moss) builds its horizontal vertex. The community of a grass, *Agrostis* and blue green alga, *Schizothrix* form cataracts¹⁴, particularly in the Lower Lakes (Tab. 1). Additionally, *Schizothrix* forms tufa coating at sprinkled surfaces and fills cavities in tufa. Accordingly, based on the dominant plant involved in tufa formation, Pevalek distinguished four types of tufa, where each one was associated with particular microrelief and flow conditions (Pevalek, 1935; Jennings, 1971; Pevalek Kozlina, 2011). Two are primarily produced by mosses (*Cratoneuron commutatum* and *Bryum pseudotriquetrum*), one by alga (*Schizothrix*), and another by grass to-

¹³ Oligotrophic lakes are characterized by the low primary production of organic matter. Generally, during the summertime, in oligotrophic lakes, the hypolimnion (with no drift) is much larger than the shallow, warm surface layer – epilimnion (with established water flow). Oligotrophic lakes are nutrient-poor. Accordingly, aquatic plants are scarce in the littoral zone and plankton blooms are rare. Due to low quantity of organic matter, the dissolved oxygen levels in oligotrophic lakes are high. Oligotrophy is found in geologically young lakes or in lakes that are not substantially affected by products of atmospheric and erosion processes. Conversely, eutrophic lakes have high primary production and consequently, they are rich in nutrients. Mesotrophic lakes are characterized by an intermediate level of primary production of organic matter.

¹⁴ Here, a barrier in the river bed that causes water to fall over it. Sometimes, the term cataract is used as a synonym of waterfall.

gether with the alga (*Agrostis* and *Schizothrix*). In other parts of the world, many other plants play similar roles in the construction of tufa barriers (*e.g.*, Jennings, 1971; Pentecost, 1981; Heery, 2007; Cantonati *et al.*, 2016).

As the face of the barrier moves downstream, colonies of *Bryum pseudotriquetrum* at the barrier vertex also move downstream, enabling the continuous growth and thickening of the barrier. Therefore, the shapes of barriers everywhere are similar, *i.e.*, at the upstream and downstream side of barrier, the slope is low and steep, respectively, while the barrier vertex is almost horizontal. Such shape is most clearly seen at inflow barriers of lakes 2, 3 and 8 (Ciginovac, Okrugljak and Galovac, respectively) and Sastavci waterfall (Petrik, 1958).

Although the precipitation of calcium carbonate from waterways is primarily a chemical process (Pentecosts, 1981, 2005), algae, bacteria and plants contribute to tufa formation. Thus, mosses serve as a substrate for deposition, while algae and numerous bacteria excrete mucus, which serves as a glue for calcite¹⁵ microcrystals and is necessary for the initiation of calcite precipitation (Emeis *et al.*, 1987; Matoničkin Kepčija *et al.*, 2006). While young shoots of mosses are green, soft and mainly without tufa, older shoots are completely covered with tufa and are calcified. Apart from favoring the formation of tufa barriers, living organisms also embed themselves into barriers (Chafetz *et al.*, 1994). Therefore, older barriers in Plitvice Lakes are typically filled with fossilized algae and mosses. Matoničkin Kepčija *et al.* (2006) found that Simuliidae¹⁶ (blackfly larvae), which produce silky secretion, contributed to tufa formation in Plitvice Lakes. Simuliids, which are present in the lotic environments of the PLA waters (*i.e.*, streams, channels and barriers), have a significant role in the initial phases of tufa deposition since their excreted silk traps and binds microcrystalline calcite, enhancing tufa barrier growth.

During the last several decades, geochemical investigations of the PLA focused on the geochemical and biogeochemical conditions and factors governing the tufa barrier growth and deposition of sediments in lakes (Fig. 21). These results are described in several studies (Matoničkin *et al.*, 1971; Srdoč *et al.*, 1982, 1985, 1986, 1987, 1994; Kempe and Emeis, 1985; Emeis *et al.*, 1987; Chafetz *et al.*, 1994; Horvatinčić *et al.*, 2000; Plenković-Moraj *et al.*, 2002; Frančičković-Bilinski *et al.*, 2004; Matoničkin Kepčija *et al.*, 2006, 2011; Golubić *et al.*, 2008; Horvatinčić, 2013). Lakes sediments (Popović *et al.*, 1986; Horvatinčić *et al.*, 1999; Obelić *et al.*, 2005; Šutić *et al.*, 2009; Krajcar Bronić *et al.*, 2010; Barešić *et al.*, 2011; Herceg Romanić, 2012) and anthropogenic pollution of lakes

¹⁵A widespread carbonate mineral. Calcite is one of the three polymorphs (forms of crystal structures) of calcium carbonate (CaCO₃). The remaining two polymorphs are the minerals aragonite and vaterite.

¹⁶Simuliids (blackfly larvae) excrete silk in the form of drift line from their labial glands. This silk pad serves as an anchor, hooking larvae to the substrate surface, which prevents larvae from drifting off and enables its feeding.

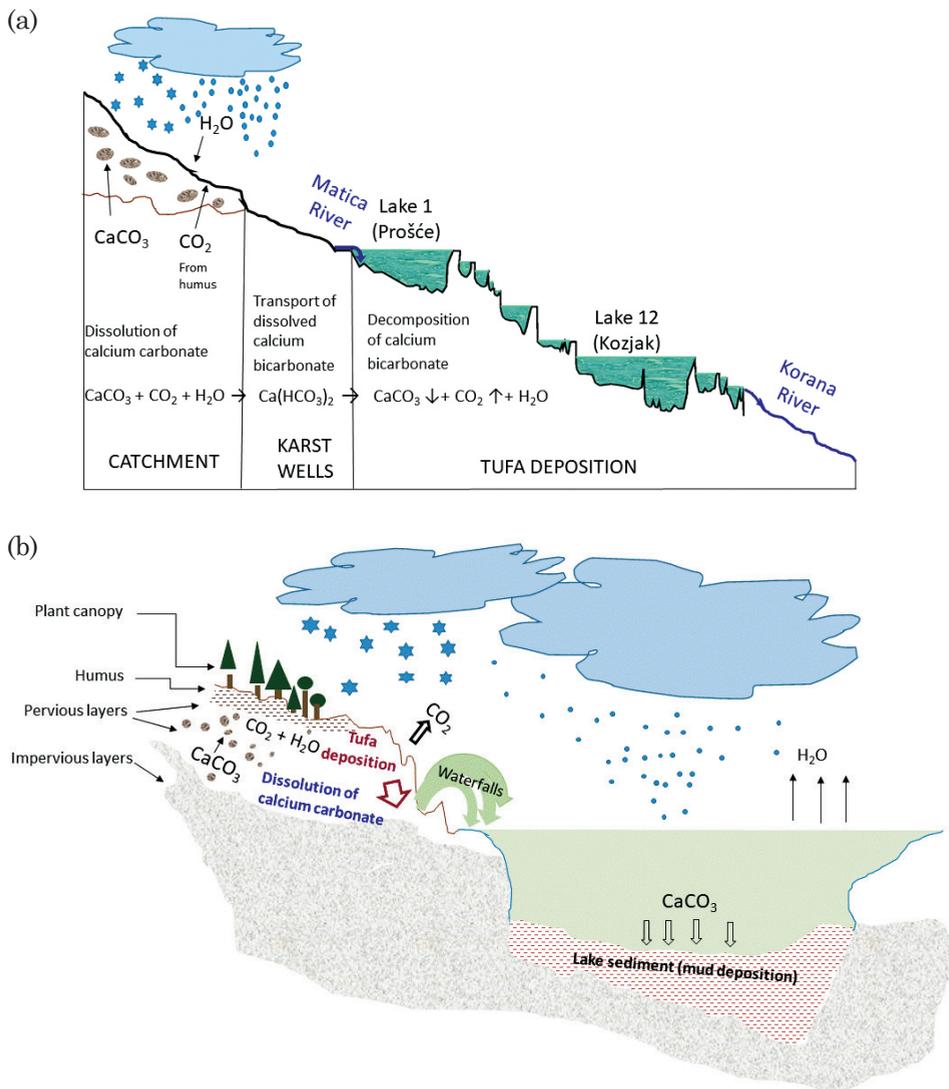


Figure 21. Geochemical processes of tufa formation (a) and deposition of lake sediments (b) (based on sketch provided by Barešić, 2009). Over the catchment area (panel a), the water (H_2O) from precipitation, while percolating through permeable upper layers, dissolves carbon dioxide (CO_2) from humus, thus forming diluted carbonic acid. This weak acid percolates further, and it dissolves calcium carbonate (CaCO_3), which is found in the upper, porous catchment limestone layer. As a result, dissolved calcium bicarbonate is formed, which is transported further and is again decomposed into calcium carbonate (which deposits) and carbon dioxide and water. Panel b shows a closer look at a single lake. Water contains dissolved calcium bicarbonate (i.e., $\text{Ca}(\text{HCO}_3)_2$) when it reaches a surface, and when it is sprayed into droplets, it releases CO_2 . Therefore, the chemical balance of water is disrupted, and the water becomes oversaturated with calcite, CaCO_3 . Therefore, calcium carbonate crystals (calcite) are formed, which are deposited in the form of tufa barriers or lake sediments (Obelić, 2011).

waters and sediments (Obelić et al., 2005; Obelić, 2006; Horvatinčić et al., 2006, 2008; Babinka, 2007; Barešić, 2009; Herceg Romanić, 2011, 2012; Mikac et al., 2011; Dautović et al., 2014; IRB, 2014; Vukosav et al., 2014) were also investigated. Among others, it was found that tufa deposition was more intense during warm climate periods, *i.e.*, interglacial periods, while it was mainly intermittent during glaciation (Srdoč et al., 1985).

The active tufa started to form approximately 6000–7000 years ago (Srdoč et al., 1985, 1986). However, within the PLA, tufa of ages between 90,000 and 130,000 years (the Riss-Würm Interglacial Stage) and between 250,000 and 300,000 years (Mindel-Riss Interglacial Stage) is found in paleo-barriers at altitudes above the current lake surfaces (Srdoč et al., 1985; Horvatinčić et al., 2000; Obelić and Horvatinčić, 2013). During ice ages, conditions were unfavorable for tufa formation, and barriers were destroyed. The transition from glacial to warmer, interglacial conditions was accompanied by the melting of ice and snow, and, consequently, by the intense flushing of surface soil layers from higher altitudes of the PLA into a lower canyon, which was corroborated by an investigation of the sediments in lakes 1 and 12 (Srdoč et al., 1985). The similar increased transport of terrigenous material also occurred in other geological regions of Croatia, from the Pannonian Basin to the Dinaric Alps. During glacial periods, the mechanical weathering of ice and water most likely deepened the Korana River riverbed. Thus, present barriers form at lower altitudes than those of older barriers. Additionally, it is known that the rates of barriers growth are not uniform. Therefore, if downstream barriers grow quicker than upstream barriers, the upstream barriers can eventually be submerged, as was already noticed by Petrik (1958). There are several submerged barriers in the Plitvice Lakes, but the most prominent one is found in Lake 12 (see Section 2).

Calcium carbonate precipitates faster in the presence of macrophytes, which form cascades. The accretion of tufa generates barriers and consequent chains of cascade lakes. Simultaneously, with the formation of barriers, carbonate silt/sediment deposits on the bottoms of the lakes (Fig. 21b). Srdoč et al. (1982, 1985, 1986, and 1987) performed radiocarbon dating of sediments in Plitvice Lakes. They concluded that sediments belonged to the Holocene and that they were predominantly formed by the deposition of calcite from the water, not from the erosion of rocks. Later, Krajcar Bronić et al. (2010) confirmed that both lake sediments and tufa of Plitvice Lakes have existed in the present form since the last Ice Age. Based on X-ray diffraction and optical microscopy Popović et al. (1986) concluded that the lake sediments are mainly composed of calcite and a small amount of dolomite or quartz. However, in Lake 1, the dominant mineral below the calcareous sediment is quartz, while rock minerals, such as feldspar, mica, chlorite and traces of calcite and dolomite, are also found. According to Barešić (2009), the share of calcite in the lake sediments is approximately 70–99%, and it increases downstream from Lake 1 (Prošće) to Lake 15 (Kaluderovac). Simultaneously, the share of organic matter in sediments, which is generally low

(2–8%) in Plitvice Lakes, decreases downstream. This result implies that there is a downstream decrease in the input of allochthonous¹⁷ organic matter. Barešić also concluded that terrigenous inputs into the Plitvice Lakes have been decreasing over the last several decades.

The deposition of sediments in the Plitvice Lakes is not a uniform process. While Lake 1 has an approximately constant sedimentation rate ($\approx 1.4 \text{ mm yr}^{-1}$), the rate for Lake 12 has been close to constant ($\approx 0.8 \text{ mm yr}^{-1}$) only during the last 3000 (Srdoč et al., 1985) or 1800 years (Srdoč et al., 1986). Babinka (2007) assessed the sedimentation rates based on gamma-spectrometric measurements of radionuclide isotopes in recent sediments (last 150 years) and by employing several sedimentation rate models, where the anthropogenic isotopes of cesium (^{134}Cs and ^{137}Cs) and natural isotopes of lead (^{210}Pb and ^{214}Pb) and bismuth (^{214}Bi) were considered. The sedimentation rates obtained from ^{137}Cs data varied between 0.5 and $1.8 \text{ kg m}^{-2} \text{ yr}^{-1}$, while ^{210}Pb data produced rates between 0.8 and $4.4 \text{ kg m}^{-2} \text{ yr}^{-1}$. Further, she found lower sedimentation rates for larger lakes (Lake 1 and Lake 12) relative to smaller lakes (Lake 10 and Lake 15). This was also confirmed by Horvatinčić et al. (2008) and Barešić (2009), who estimated that sedimentation in lakes 10 and 15 was $3\text{--}4$ times faster than that in larger lakes.

Tufa barriers grow at different rates than lake sediments are deposited. By comparing the lakes levels measured in 1855 with his measurements, Petrik (1958) estimated that the average barrier growth rate was approximately 1 to 3 cm yr^{-1} . Later, based on radiocarbon (radioactive isotope of carbon, ^{14}C) dating, Srdoč et al. (1985) calculated a value of 1.35 cm yr^{-1} . However, recent hydrological analyses of water levels and discharges during the period of 1952–1990 (Rubinić et al., 2008) suggested noticeably different growth rates of tufa barriers for the two largest lakes, *i.e.*, 0.56 cm yr^{-1} and approximately 1.5 cm yr^{-1} for the Lake 12 and Lake 1, respectively.

Apart from the oversaturation of water with calcium carbonate and the contribution of living organisms, other important factors that affect the tufa formation include (Srdoč et al., 1985) water velocity in the range $0.5\text{--}3.5 \text{ m s}^{-1}$ and pH of water above 8 (at locations with intense calcite precipitation, pH was most frequently between 8.2 and 8.4). Further, the concentration of dissolved organic matter (DOM), and accordingly, the concentration of dissolved organic carbon (DOC) should be low (DOC below 10 mg l^{-1}). Tufa deposition (Fig. 21) is the result of two processes. One of them is the inorganic release of CO_2 from the water due to the heating of the water or due to a drop in CO_2 pressure, which is caused by

¹⁷ Allochthonous organic matter originates from outside the aquatic system. That is, the products of incomplete decomposition of plant and animal remains from the catchment area are carried into the aquatic system by wind or flushing due to precipitation. On the other hand, autochthons organic matter forms in the aquatic system due to photosynthesis and the destruction of detritus (dead bacteria, phytoplankton and animal bodies) (*e.g.*, Lozovik et al., 2007).

increased turbulence and effective degassing of CO₂ at waterfalls. The other is the organic removal of CO₂ from the water by biological photo-synthetic processes of aquatic plants, algae and cyanobacteria. For tufa deposition in the Plitvice Lakes, biological processes are much more important than are inorganic CO₂ degassing processes (Chafetz et al., 1994).

Recently, Sironić et al. (2017) addressed the influence of changing climatic conditions on tufa deposition process. Namely, they compared two periods, 1981–1986 and 2010–2014, and they found that the mean air temperature in Gospić (which is approximately 25 km far from the PLA) for the second period was approximately 2 °C higher than that of the first period. Similarly, the average water temperatures for the second period were 1.5 °C (lakes), 0.6 °C (spring of *Bijela rijeka*), and 0.4 °C (spring of *Crna rijeka*) higher than those for the first period. The increase in the air and water temperatures between these two periods was accompanied by an increase in the concentrations of dissolved calcium and hydrogencarbonate ions (Ca²⁺ and HCO₃⁻, respectively) in water. However, for both periods, the downstream decrease in HCO₃⁻ was almost the same, which indicated that the entire karst lake system acts as a carbon sink. The increase of Ca²⁺ and HCO₃⁻ concentrations, which was observed over the last three decades in waters of all eight inspected locations in the PLA, was mainly caused by an increase in these values at springs. The increase in the Ca²⁺ and HCO₃⁻ concentrations (which was also observed at springs in the Alps and the eastern Balkan karst area) is most likely caused by increased limestone dissolution in springs, where the dissolution of limestone is most likely enhanced due to enhanced bioproductivity on relatively impermeable dolomite bedrock and enhanced degradation of organic matter at limestone bedrock locations.

Newer investigations of physical and chemical characteristics of waters

More recent investigations of the physical and chemical characteristics of waters of the PLA were performed for different seasons. They included main springs (*Crna rijeka*, *Bijela rijeka* and Plitvica with Sartuk Brook), tributaries (Matica and Rječica) and outflowing Korana River (Barešić, 2009; Barešić et al., 2011; Horvatinčić, 2013; Barešić and Krajcar Bronić, 2017) and Lake 1 (Prošće), Lake 10 (Gradinsko), Lake 12 (Kozjak) and Lake 15 (Kaluderovac) (Horvatinčić et al., 2006). They revealed both noticeable differences among spring, lake and stream waters and steady downstream changes in measured parameters. Lake water was characterized by high seasonal variations in surface temperature (up to approximately 20 °C), while the temperatures of the three main springs were steady (7.1–8.1 °C) throughout the year. Furthermore, the pH values of springs and downstream lakes varied between 7.3 and 7.6 and between 8.2 and 8.6, respectively. While the pH values of water increased downstream, the concentration of hydrogencarbonates, which are the main components of dissolved inorganic carbon (hereafter, DIC), decreased from 4.5 to 3.5 mmol l⁻¹. The concentration of CO₂ also gradually decreased down-stream. On the other hand,

the concentration of DOC was the lowest in spring water, while the highest values were found for one location in Lake 12 and in Lake 1. For the other sampling sites, DOC slightly decreased downstream. The DOC, which had elevated values in the uppermost Lake 1 relative to the main springs, was attributed to the Matica River, which passes through peat bogs, and thus, brings additional DOC to Lake 1. The elevated DOC in Lake 12 was due to the input of foliage and other organic matter by the Rječica River.

The authors also calculated the saturation index (I_{sat}) of CaCO_3 :

$$I_{sat} = IAP / K, \quad (9)$$

where IAP is the ion activity product and K is the solubility product. In lake portions where the precipitation of calcite was intense, the values of I_{sat} were high (between 4 and 10), showing that water was oversaturated with calcium carbonate; in contrast, in spring and tributary waters, values were lower (between 1 and 2). This result agrees fairly well with the previous results of Srdoč et al. (1985), who emphasized that one of the conditions necessary for abundant calcite precipitation is $I_{sat} > 3$ and that the intense precipitation of calcite is found at locations with I_{sat} between 5 and 7.

Apart from Plitvica Brook (Mejaški et al., 2016), in springs and tributary stream waters, calcite does not precipitate even if the water is oversaturated with calcite. Dautović et al. (2014) reported on the physico-chemical conditions of the PLA waters. In springs (pH from 7.3 to 7.9, high level of dissolved CO_2 and low $I_{sat} \approx 1$), conditions are not favorable for calcite precipitation. On the other hand, these conditions are appropriate in tributaries (pH from 8.0 to 8.8, I_{sat} from 2 to 18). Apart from steady temperatures, generally lower I_{sat} values and lower pH values, springs and tributaries are also characterized by high concentrations of hydrogencarbonate (from 4.2 to 5.2 mmol l^{-1}) and CO_2 (0.2–0.7 mmol l^{-1}) relative to downstream lakes. Barešić et al. (2011) hypothesized that calcite did not precipitate due to the input of allochthonous materials (*i.e.*, due to DOC). Similarly, in the very upper course of the Korana River (next to Lake 16), there is no tufa deposition despite of the fact that there is oversaturation of water with calcium carbonate, which is again due to the high concentrations of DOC. Conversely, for Plitvica Brook, Meaški et al. (2016) recently reported on the formation of tufa barriers, which is very intense at some locations. Therefore, they concluded that from a hydrogeological perspective, the Plitvica watercourse corresponds to the spatially reduced system of Plitvice Lakes.

Springs and lakes also differ in water hardness, which is higher in springs. Vurnek et al. (2010) examined total, calcium and magnesium hardness for *Bijela rijeka*, *Crna rijeka* and *Kozjak*. For total hardness, they obtained following averages: 276.88 $\text{mg CaCO}_3 \text{ l}^{-1}$ (source of *Bijela rijeka*), 271.96 $\text{mg CaCO}_3 \text{ l}^{-1}$ (downstream point of *Bijela rijeka*, source of *Crna rijeka* and downstream point of *Crna rijeka*), and 219.64 $\text{mg CaCO}_3 \text{ l}^{-1}$ (Lake 12). The authors concluded that the

lower lake water hardness was most likely due to downstream calcite precipitation.

While it is known that DOM (and accordingly, DOC) inhibits calcite precipitation, the possible role of suspended matter in tufa growth is not yet understood in the Plitvice Lakes. The study by Špoljar et al., (2007) may serve as a starting point for future investigations on the role of suspended matter in tufa formation. The authors measured the total suspended matter (TSM), particulate inorganic matter (PIM), particulate organic matter (POM), chlorophyll-a, heterotrophic bacteria and water discharge, and afterwards, they calculated seston¹⁸ transport. They measured the variables listed above at three distinctive sections of the Plitvice Lakes: a channel with a low inclination (Labudovac Channel), a deep lake (from Lake 5 barrier to Lake 8 barrier), and a channel with cascades and high inclination (between the two barriers of Lake 13). The authors obtained significant negative correlations between the observed matters and discharges. Differences in the net seston transport were the highest between the deep lake section and the section with the steep inclination, which was also where the differences in TSM and PIM were most prominent. In comparison with worldwide values for purely lotic systems (which are characterized by much higher discharges), seston transport in the Plitvice Lakes is generally low. This result is due to both the low discharges (6–9 m³ s⁻¹) and the low trophic state of the lakes.

Barešić et al. (2011) studied the $\delta^{13}\text{C}$ values¹⁹. For lake water, where the precipitation of calcite was intense, they found a positive correlation between the pH values and I_{sat} (correlation coefficient $r = 0.87$) and a negative correlation between the pH values and hydrogencarbonate anion (HCO_3^-) concentrations²⁰ ($r = -0.45$), which they attributed to CO_2 degassing²¹ and the decomposition of calcium bicarbonate (and consequent calcite precipitation). Furthermore, $\delta^{13}\text{C}_{\text{DIC}}$ gradually increased downstream, with an average value of -12.7‰ and -8.6‰ in springs and in the Korana River, respectively. The authors also found a negative correlation ($r = -0.65$) between the concentrations of HCO_3^- and $\delta^{13}\text{C}_{\text{DIC}}$, which they attributed to CO_2 degassing, calcite deposition and biological activity of aquatic algae and macrophytes associated with photosynthesis. While seasonal variations in $\delta^{13}\text{C}_{\text{DIC}}$ were found in lake water (which exhibited seasonal variations in temperature), these were not found in spring water (which had

¹⁸ Seston is composed of inorganic particles and dead or living (such as plankton) organic particles. Conversely to DOC or DIC, seston is undissolved.

¹⁹ $\delta^{13}\text{C}$ value depends on the ratio of the stable carbon isotopes ^{13}C and ^{12}C . It is calculated from $\delta^{13}\text{C} = 1000 \cdot [(R_{\text{sample}} / R_{\text{standard}}) - 1]$, where $R_{\text{sample}} = (^{13}\text{C} / ^{12}\text{C})_{\text{sample}}$ and $R_{\text{standard}} = (^{13}\text{C} / ^{12}\text{C})_{\text{standard}}$. $\delta^{13}\text{C}$ is in per mill (‰).

²⁰ In the Conclusions of the article by Barešić et al. (2011), it was erroneously written that correlation coefficient $r = -0.45$ corresponds to pH and $\delta^{13}\text{C}_{\text{DIC}}$, instead of pH and HCO_3^- (Barešić et al., 2018).

²¹ Removal of CO_2 from the water.

mainly constant temperatures throughout the year). Finally, a downstream increase in $\delta^{13}\text{C}_{\text{DIC}}$ in waters was accompanied by a downstream increase in $\delta^{13}\text{C}$ for calcite in the lake sediments, which suggests that precipitated calcite is mainly of autochthonous origin.

Biondić et al. (2007, 2008, 2010, 2016, 2017) and Meaški (2011) performed complex investigations of the PLA that addressed the sustainable utilization and protection of the PLA waters. In addition to conventional hydrogeological methods, they used new methodologies, such as remote sensing, groundwater tracing techniques and hydrogeochemical modeling, which was based on environmental isotopes and major and trace dissolved solute data. They also applied geographic information system (GIS) mapping technology. Apart from the hydrological results, which have already been described in Section 4, the authors assessed the vulnerability and risks that endanger the direct catchment of the Plitvice Lakes. They made a map of erosion, which highlighted the expected directions of transport of eroded materials, such as pelite²² material, foliage and other organic matter, since these may endanger the ecological state of the lakes.

Mean residence time (MRT)

Some studies investigated the mean residence time (hereafter, MRT) of water (Srdoč et al., 1985; INCO, 2005; ANTHROPOL.PROT, 2006; Babinka, 2007, 2008). The concept of MRT assumes that water is a mixture of water parcels of different ages and that the mixture is well defined (e.g., Babinka, 2007). In isotope hydrology, MRT is frequently assessed using lump parameter models (hereafter, LPMs) (Maloszewski and Zuber, 1996). These models (also known as black-box models) describe groundwater systems using a small number of parameters. LPMs consider the entire groundwater system as a single structure, and they assume that the flow through this system is steady. Furthermore, they describe the relative contribution of water parcels of certain age using a convolution integral:

$$C_{out}(t) = \int_{-\infty}^t C_{in}(t') \cdot g(t-t') \cdot e^{-\lambda(t-t')} dt' \quad (10)$$

where $C_{out}(t)$ is the output concentration of a particular tracer sampled at a well or spring, $C_{in}(t')$ is the input concentration of the tracer, t' is the time of entry, $g(t-t')$ is a weighting function for the water found in the mixed sample whose age is $(t-t')$, and $e^{-\lambda(t-t')}$ is the radioactive decay. The difference between the various LPMs is in selection of the weighting function g , which is a function of water age (i.e., the function of the time difference between the infiltration and output times). While one-component models consider a water sample as a sample of a single age, two-component models describe the sample as a mixture of two

²² Pelite is the finest grained clastic sediment composed of grains with a size < 0.0625 mm.

waters of different ages. Some of the one-component LPMs include the piston flow model (PFM), exponential model (EM), dispersion model (DM) and linear model (LM), while two-component models are a combination of two one-component models, such as a piston flow-dispersion model (PFMDM) and piston flow-exponential model (PFMEM). The PFM assumes that new water masses that enter an aquifer system suppress the present water without any mixing or hydrodynamic dispersion²³ or molecular diffusion²⁴. Conversely, the EM presumes the mixing of new water with the water that is already present in the system. That is, the EM considers a water sample as an ideal mixture, which has an exponential age distribution. The DM considers the water transport to be “smeared” by dispersion-like processes, and it employs the Péclet number:

$$Pe = l \cdot v / d, \quad (11)$$

where l is the characteristic length of the system, v is the advection velocity and d is the dispersion coefficient. Finally, the LM assumes that the distribution of transit times of a tracer is constant. The mean transit time of a tracer (t_t), which is also known as the mean age of the tracer, is defined as (Maloszewski and Zuber, 1996):

$$t_t = \int_0^{\infty} t C_I(t) dt / \int_0^{\infty} C_I(t) dt, \quad (12)$$

where $C_I(t)$ is the tracer concentration observed at the measuring point as the result of an instantaneous injection of the tracer at the injection point at the time $t = 0$.

Srdoč et al. (1985) applied the EM. They assumed the following: 1) an aquifer fills at the same rate at which it loses water from the outflow 2) the isotope composition of a well and aquifer is the same; 3) new water quickly mixes with water already present in the aquifer; and 4) isotope composition changes only due to inflow, outflow and radioactive decay. Based on analyzed tritium²⁵ activity, they estimated the MRTs of aquifers that feed three major karst wells, *i.e.*, *Crna rijeka*, *Bijela rijeka* and *Plitvica well* (Tab. 8). Prominent differences in the

²³ Hydrodynamic dispersion (mechanical dispersion) is caused by groundwater moving with different velocities at different points. Spatial variations in groundwater velocity are caused by several reasons: fluids are moving faster through the centers of pores than along the pore edges; fluids splitting into branches (travel pathways of different lengths); and fluids moving faster through larger pores than through smaller pores. Thus, a solute that is present in the groundwater (or in any other advecting fluid), is spread and mixed along the flow path due to the spatial variations in the advecting fluid velocity. Hydrodynamic dispersion is a macroscopic phenomenon, and it is composed of the longitudinal (along the flow) and lateral (perpendicular to the flow) spreading of a solute. These are also called longitudinal and lateral dispersions, respectively.

²⁴ Transport of matter solely by the random motions of individual molecules. It is a thermal motion of all fluid particles at temperatures above 0 K.

²⁵ Tritium (³H) is a radioactive isotope of hydrogen. Its nucleus contains one proton and two neutrons.

MRT values at the three wells were attributed to the differences in the hydrogeological characteristics of the three aquifers (different porosities and consequently, different retention capacities). Water at the *Bijela rijeka* spring was “the oldest” since the retention capacity of the area was high due to the high share of dolomite and Quaternary diluvial cover. Conversely, the watershed of the *Crna rijeka* spring comprises limestone Jurassic sediments and, consequently, has a low retention capacity. Therefore, the exchange of the groundwater in the aquifer is fast. On the other hand, characteristics of the watershed of Plitvica spring are between these two. The authors concluded that the MRT of karst water is generally very short, with an average between 1 and 4 years. Furthermore, the weather conditions can substantially affect the MRT. Thus, extremely dry periods can redouble the MRT, while abundant springtime precipitation can noticeably shorten the MRT. However, Srdoč et al. noted that the applicability of the EM is less appropriate for drought periods since the filling of an aquifer is not equal to the discharge losses (*i.e.*, condition 1 is not fulfilled).

Table 8. MRTs (in years) of water in aquifers that feed the springs of *Crna rijeka*, *Bijela rijeka* and *Plitvica*, as obtained by the EM for three different periods (Srdoč et al., 1985).

Spring	Average MRT 1976–1982	MRT Low waters due to exceptionally dry period Summer and fall of 1983	MRT High waters due to snow melting Spring of 1984
<i>Crna rijeka</i>	2	4	<1
<i>Bijela rijeka</i>	4	7–8	4
Plitvica	3	5–6	1

The MRT was also investigated as part of comprehensive study on the groundwater flow dynamics, water balance, and aquifer storage capacity of the PLA within the ANTHROPOL.PROT project (Babinka et al., 2005; ANTHROPOL.PROT, 2006; Babinka, 2007, 2008). Due to the complexity of the karst system, several tracers were followed in both water and lake sediments, and isotope-hydrological, geochemical and geochronological methods were applied. Among the tracers, stable isotopes of oxygen (^{18}O), hydrogen (^2H and ^3H), noble gases helium (^3He and ^4He) and neon (^{20}Ne and ^{22}Ne), sulfur hexafluoride (SF_6), and chlorofluorocarbons²⁶ (hereafter, CFCs), namely, trichlorofluoromethane²⁷ CFC-11,

²⁶ Chlorofluorocarbons (CFCs) are hydrocarbons that contain carbon (C), chlorine (Cl) and fluorine (F). They are also known as freons. Many CFCs were used in refrigerators, in aerosols or as solvents, but due to their role in ozone depletion in the stratosphere, they were withdrawn from use by international agreement.

²⁷ Trichlorofluoromethane is also called freon-11, CFC-11, or R-11 and is a colorless chlorofluorocarbon with a chemical formula of CCl_3F .

dichlorodifluoromethane²⁸ CFC-12 and trichlorotrifluoroethane²⁹ CFC-113), were analyzed. Among the LPMs, the EM, DM, PFMDM and PFMEM were used, and the obtained results are listed in Tab. 9.

Table 9. Modeled MRT (in years). Pe is the Péclet number (Eq. 11). Water in the conduit network is denoted by c , while p corresponds to the water in the fissured-porous karst aquifer. Percentages of the young water component in the conduit network and the old water component in the karst fissured-porous aquifer are indicated by r_c and r_p , respectively (Babinka, 2007).

Spring	LPM	Pe	MRT (years)					
			Wet season and high spring discharge			Dry season and low spring discharge		
			c	p	c	p	r_c	r_p
Plitvica	EM	–	0	4	0	13.5	0	100
Crna rijeka	DM	3	0	6	0	20	0	100
Bijela rijeka	PFMDM	2.5	0.4	3	0.4	28	10	90

The investigations by Babinka (2007, 2008) also provided estimations of lake evaporation under two hydrologically different conditions (see Tab. 5a, Section 4), and they revealed the water evaporative ²H-enrichment along the lake chain from the inflow at Matica River towards the outflow of the Korana River, which is seen from the $\delta^2\text{H}$ values³⁰ during the summer months. Namely, the $\delta^2\text{H}$ values increase downstream (they become less negative), which means that water becomes increasingly enriched in deuterium (²H); furthermore, the lighter hydrogen ion, protium (¹H), escapes to the atmosphere (water molecules with protium instead of deuterium are lighter and, therefore, evaporate more readily than do heavier molecules with deuterium). However, the author did not find downstream ²H-enrichment during the winter months (*i.e.*, January–March).

Anthropogenic pollution of sediments

A number of studies have inspected the anthropogenic pollution of sediments and waters of the PLA (Horvatinčić et al., 2004; 2006; Babinka, 2007; Barešić (2009); Herceg Romanić, 2011, 2012; Mikac et al., 2011; Dautović et al., 2014;

²⁸ Dichlorodifluoromethane is also known as freon-12 or CFC-12. It is a chlorofluorocarbon with a chemical formula of CCl_2F_2 .

²⁹ Trichlorotrifluoroethane is also known as CFC-113. It is a chlorofluorocarbon with the chemical formula $\text{C}_2\text{Cl}_3\text{F}_3$.

³⁰ $\delta^2\text{H}$ value depends on the ratio of the stable hydrogen isotopes ²H and ¹H. It is calculated from $\delta^2\text{H} = 1000 \cdot [R_{\text{sample}}/R_{\text{standard}} - 1]$, where $R_{\text{sample}} = (^2\text{H} / ^1\text{H})_{\text{sample}}$, $R_{\text{standard}} = (^2\text{H} / ^1\text{H})_{\text{standard}}$, and $\delta^2\text{H}$ is in per mill (‰). In the studies of Babinka (2007, 2008), the standard value R_{standard} corresponds to VSMOW.

Vukosav et al., 2014). Babinka (2007) found elevated concentrations of detergent-derived chemicals (linear alkylbenzene sulphonates, LASs) in sediments of Kozjak that were deposited between 2000 and 2003. The author concluded that LASs, which can generally speed up eutrophication, were most likely caused by the malfunction of the sewage systems of nearby hotels. Mikac et al. (2011) corroborated this hypothesis. While the maximum LAS concentrations in the Lake 12 sediments (deposited during the year 2003) were up to 4.7 mg kg^{-1} , they were noticeably lower (up to 1.3 mg kg^{-1}) in Lake 1, which indicates there is a pollution source near Lake 12. Based on the $\delta^{13}\text{C}$ (see footnote 19) values in the carbonate and organic sediment shares (*i.e.*, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$), the $\delta^{15}\text{N}$ values³¹ in sediments ($\delta^{15}\text{N}_{\text{tot}}$) and the ratio of carbon and nitrogen (C/N) in sediments Barešić (2009) concluded that these mainly point to natural processes of the decomposition of organic matter (OM) and calcite deposition, which are typical for oligotrophic karst lakes. However, the results also point to a certain increase in primary production in last 20–30 years, which Barešić attributed to an increase in lake temperatures by 1–2 °C within last two decades. The $\delta^{13}\text{C}$ values and the ratio C/N in the organic fraction of sediment suggest that the OM in lake sediments is mainly autochthonous (created by primary production in a lake). Furthermore, the concentrations of trace elements in sediments principally point to natural sources (Horvatinčić et al., 2006; Barešić, 2009; Mikac et al., 2011). According to Horvatinčić et al. (2006), there is no significant difference among the trace elements concentrations in the newer sediments (corresponding to the last 50 years, when higher anthropogenic influence can be expected due to increasing tourist activities) and older sediments (corresponding to 100–200 years prior to present day) (Horvatinčić et al., 2006). Dautović et al. (2014) obtained similar results. Namely, the average concentrations of arsenic, chromium, nickel, copper and lead (As, Cr, Ni, Cu and Pb, respectively) in lake sediments were relatively low and of the same order of magnitude as the average concentrations of these substances in the pre-industrial sediments of remote Alpine and Arctic lakes. Conversely, cadmium (Cd) had concentrations above those observed in the contemporary sediments of remote lakes. Barešić (2009) concluded that Cd in the Lake 1 and the mouth of Rječica into Lake 12 sediments might be of anthropogenic origin. Similarly, traces of zinc (Zn), lead (Pb) and manganese (Mn) may have partially originated from traffic. The most recent sediments have higher Pb concentrations than do the older layers, and these remained elevated despite the gradual phasing-out of leaded fuel that began in 1995. Additionally, the amount of Pb in sediments was positively correlated with polycyclic aromatic hydrocarbons (PAHs), which indicates that they are of the same origin, *i.e.*, fossil fuels (Mikac et al., 2011). The concentrations of most trace elements (Mn, Fe,

³¹ $\delta^{15}\text{N}$ value depends on the ratio of stable nitrogen isotopes ^{15}N and ^{14}N . It is calculated from $\delta^{15}\text{N} = 1000 \cdot [(R_{\text{sample}} / R_{\text{standard}}) - 1]$, where $R_{\text{sample}} = (^{15}\text{N} / ^{14}\text{N})_{\text{sample}}$, $R_{\text{standard}} = (^{15}\text{N} / ^{14}\text{N})_{\text{standard}}$, and $\delta^{15}\text{N}$ is in per mill (‰).

Al, Cd, Zn, Cu, Ni, Pb, Co, Cr and Tl)³² in sediments decreased downstream from the sources to the lakes (Dautović et al., 2014). This result indicates an efficient removal of dissolved elements, which is mainly due to co-precipitation with authigenic calcite³³ and Mn oxides. Finally, most of the trace elements in lake sediments were highly correlated with aluminum (Al), which suggests their terrigenous origin. This is in accordance with previous findings (Horvatinčić et al., 2006; Barešić, 2009; Mikac et al., 2011) that found the trace elements in lakes sediments were mainly of natural origin. Finally, Vukosav et al. (2014) reported on the anthropogenic influence on Lake 12 (Kozjak) sediments, where mercury (Hg) concentrations were up to four times higher than the baseline³⁴ value, while Pb at two locations exceeded the probable effect concentration³⁵ (PEC), which, for lead, is $PEC(Pb) = 128 \mu\text{g g}^{-1}$ (MacDonald et al., 2000). Extremely high contents of Pb in sediments were found in the upper part of Lake 12, which is the most exposed to tourists. The authors hypothesized that Pb originated from gasoline and that it was transported to Lake 12 by the Rječica River, whose watercourse is roughly parallel to the nearby ($\approx 1\text{--}1.2$ km distant) motorway, which has dense traffic. Still, elevated Hg and Pb concentrations were not found in fish tissues. However, the authors found a significant correlation between the Cd levels in fish liver and muscle and the Cd in sediments. Vukosav et al. concluded that, apart from extremely elevated Pb in the sediments of upper part of Lake 12, metal levels in the surface sediments of Plitvice Lakes corresponded to those of clean, natural systems.

Nuclear weapon testing in the 1950s and 1960s and the Chernobyl accident in 1986 also left signatures in the lake sediments (Babinka, 2007; Horvatinčić et al., 2008; Barešić, 2009, Barešić et al., 2011a). Thus, Babinka (2007) found a peak in radioactivity for the radioactive isotope of cesium (^{137}Cs) in Lake 1 sediment at a depth of 8.5 cm, which she attributed to Chernobyl fallout. For Lake 10 (Gradinsko), she found two ^{137}Cs peaks, one at a sediment depth of 7 cm and the other at 14 cm, which, according to author, correspond to Chernobyl in 1986 and a nuclear bomb fallout in 1963, respectively. Similarly,

³²Trace elements are chemical elements that occur in very small amounts in a particular sample of environment. Namely, manganese (Mn), iron (Fe), aluminum (Al), cadmium (Cd), zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), cobalt (Co), chromium (Cr) and thallium (Tl).

³³Authigenic minerals, such as calcite, halite and gypsum, form in situ where they deposit due to geochemical processes. Conversely, detrital materials, such as grains of quartz and feldspar, are resistant to weathering, and they are transported to a deposition site.

³⁴Baseline metal concentrations in sediments are of natural origin and they exhibit natural variations (Newman and Watling, 2007). They are differentiated from man-made concentrations by geochemical normalization methods, as described in Kersten and Smedes (2002).

³⁵Probable effect concentration (PEC) is the concentration above which adverse effects are expected to frequently occur (MacDonald et al., 2000).

Barešić (2009) observed a peak in the relative specific activity³⁶ ($a^{14}\text{C}$) in Lake 10 sediments at the depth of 14 cm, which she also attributed to thermonuclear explosions.

Water pollution

Numerous authors have concluded that waters of the Plitvice Lakes are clean and oligotrophic, with no significant indications of anthropogenic pollution (Horvatinčić et al., 2006; Barešić, 2009; Dautović et al., 2014; Dražina et al., 2014; Vukosav et al., 2014). Horvatinčić et al. (2006) analyzed waters of two main springs (*Crna rijeka* and *Bijela rijeka*) and four lakes (1, 10, 12 and 15, *i.e.*, Prošće, Gradinsko, Kozjak and Kaluđerovac, where samples for Lake 12 were taken at two sampling sites). They collected surface water samples seasonally during 2003–2004, and they measured water temperature, pH, conductivity and dissolved oxygen *in situ*, while the trace elements (B, Al, Cr, Sr, Mn, Fe, Ni, Cu, Zn, Cd, Ba, Pb and P)³⁷, anions (SO_4^{2-} , Cl^- , F^- , NO_3^- , NO_2^- , HPO_4^{2-})³⁸ and DOC were determined in a laboratory. The authors concluded that there was no significant anthropogenic pollution of water since the concentrations of trace elements were below detection limits. The somewhat higher concentrations of nitrates and ammonia in spring waters and at one sampling site in Lake 12 point to natural origin, such as the percolation of groundwater through humus and transport from wooded environments by surface waters. Finally, the concentrations of DOC and nutrients were somewhat higher for the sampling site in Lake 12, which corresponded to the area of increased eutrophication-plant growth. Barešić (2009) reached a similar conclusion. She performed physico-chemical measurements of surface and percolating water. The author found that the main nutrient source for lakes was percolated water and that the waters of the Plitvice Lakes were clear and oligotrophic, without significant anthropogenic pollution.

Recently, Dautović et al. (2014) showed that the precipitation of authigenic calcite (see footnote 33) in lakes is an important mechanism for the removal of trace metals from lake waters. That is, a multi-cascade lake system enhances the autopurification efficiency by eliminating most of the trace metals from the aqueous phase. Vukosav et al. (2014) showed that the concentrations of trace metals (Cd, Cu, Pb, Zn and Hg) in waters of PLA are very low and comparable to the concentrations found in unpolluted waters of other protected karst areas;

³⁶Relative specific activity $a^{14}\text{C}$ is defined as the ratio of the specific activity of the sample and of the atmosphere that is undisturbed by anthropogenic influences (Obelić et al., 2010). It is expressed in percents of Modern Carbon (pMC). Thus, for example, $a^{14}\text{C} = 100$ pMC corresponds to a specific activity of $226 \text{ Bq (kg C)}^{-1}$ or to the $^{14}\text{CO}_2$ activity concentration of 0.037 Bq m^{-3} of air.

³⁷That is, boron (B), aluminum (Al), chromium (Cr), strontium (Sr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), barium (Ba), lead (Pb) and phosphorus (P).

³⁸That is, sulfate ion (SO_4^{2-}), chloride ion (Cl^-), fluoride ion (F^-), nitrate ion (NO_3^-), nitrite ion (NO_2^-), and hydrogen phosphate ion (HPO_4^{2-}).

furthermore, the concentrations were far below the limits provided by the European Union Environmental Quality Standards Directive (EIONET, 2018). They found slightly increased metal concentrations for the waters of *Bijela rijeka* (Cd up to 50 ng l^{-1} and Zn up to 900) and *Crna rijeka* (Cd up to 25 ng l^{-1}), but they were of natural origin. Downstream of these two watercourses, due to the auto-purification of water at tufa barriers, as already explained by Dautović et al. (2014), the levels of metals in the waters were uniform and low. Finally, Vukosav et al. (2014) found a significant correlation between Cd levels in fish liver and muscle and concentrations of Cd in water. Dražina et al. (2014) also confirmed that the waters of the Plitvice Lakes are clean and oligotrophic. The authors investigated a constantly submerged microhabitat of the last tufa barrier, which divides the lakes 15 and 16 (Kaluderovac and *Novakovića brod*) and is close to the source of the Korana River. The nematode (roundworms) species found and their community composition indicate unpolluted water of a low trophic state.

However, Vurnek et al. (2010), who examined the presence of aerobic heterotrophs as well as the total and fecal coliform bacteria in waters during the 2006–2008 period, reported on the bacteriological pollution of *Bijela rijeka*. The level of pollution depended on the hydrological conditions, and pollution was elevated during periods of low water. The highest total coliform bacteria concentration in *Bijela rijeka* was observed in July 2006 ($\approx 8800 \text{ l}^{-1}$). Bacteria concentrations decreased downstream, and by the Kozjak Bridge location, they stabilized at very low values, indicating that the lake system is large and stable enough to neutralize such pollution. Nevertheless, they point to the importance of recovery and preservation of water quality in the *Bijela rijeka* watershed.

Herceg Romanić (2011; 2012) and Brozinčević et al. (2017), also investigated water quality. Preliminary reports of Herceg Romanić on the organic and inorganic pollution of waters in the PLA show the presence of pesticides and the volatile organic compounds, *i.e.*, benzene, toluene, ethylbenzene and xylene (BTEX³⁹). However, the levels of observed pesticides and the BTEX concentrations were lower than limit values set by Croatian (and European Union) legislation.

Soil pollution

Miko et al. (2001) and Halamić and Miko (2009) performed geochemical investigations of the soil of the PLA to produce the Geochemical Atlas of Croatia (Miko et al., 2001; Halamić and Miko, 2009). However, their results correspond-

³⁹ BTEX (benzene, toluene, ethylbenzene and xylene) are volatile organic compounds that occur naturally in crude oil. They can be found in seawater in the vicinity of natural gas and petroleum deposits. They are also emitted from volcanoes and forest fires. Major anthropogenic sources of BTEX are motor vehicles, aircrafts and cigarette smoke. They are also emitted during the processing of petroleum products and during the production of paints, lacquers, thinners, rubber products, inks, adhesives, cosmetic products, and pharmaceutical products. BTEX compounds are among the most abundantly produced chemicals in the world.

ed to the entire Croatian territory, and thus, they are available as a coarse resolution raster. Recently, Heceg Romanić et al. (2016) studied the anthropogenic pollution of the PLA soil. The authors inspected the distributions of organic contaminants, major and trace elements, and biological indicators of air contamination (*i.e.*, conifer needles, mosses, and lichens). They concluded that the analyzed trace elements generally pointed to natural sources. Anthropogenic radionuclides in biological indicators exhibited low but measurable activity of the cesium radioisotope ^{134}Cs for the first time after the Chernobyl accident in 1986, which was attributed to the Fukushima nuclear power plant accident in March 2011. Overall, the authors did not find any significant impact of human activity top soils in PLA.

6. Physical limnology

Previous investigations of the Plitvice Lakes showed that the lake water temperatures affected the primary production in the lakes (*e.g.*, Barešić, 2009) and the tufa deposition (*e.g.*, Sironić et al., 2017) processes. Tufa deposition also depends on turbulence and mechanical mixing in lakes (*e.g.*, Chen et al., 2004; Florsheim et al., 2013). Further, several studies of the Plitvice Lakes confirmed that water velocity also substantially influenced phenomena, states and processes that are important for tufa formation, *e.g.*, distribution of suspended matter (*e.g.*, Špoljar et al., 2007) and living organisms (*e.g.*, Matoničkin Kepčija, 2011; Sertić Perić et al., 2014, 2015) and the decomposition of leaves (Belančić et al., 2009). While several studies have reported on the lake temperatures and their distribution, the movement of water within lakes has been poorly investigated.

Lakes temperatures and stratification

The Plitvice Lakes are dimictic (*e.g.*, Babinka 2007; Špoljar et al., 2007). This means that they mix from the surface to the bottom twice each year⁴⁰. They are stratified in summer, and they mix in fall and spring. Gavazzi (1919) was the first to publish observed lakes temperatures. On several occasions, the author measured the surface temperature of lakes 1, 8 and 12 (Prošće, Galovac and Kozjak, respectively) at points adjacent to the lakeshore. He noted that the lake surface temperatures in regions of stagnant water were substantially higher (up to 1 °C) than those measured in areas where water moved. Gavazzi also reported on diurnal variations in the lake surface temperatures (Fig. 22.). He perceived that the minimum lake surface temperature occurred approximately 1 hour after the sunrise, *i.e.*, much later than the minimum air temperature,

⁴⁰ Conversely, in meromictic lakes, deep recirculation does not encompass the entire water body. Thus, they are permanently stratified (*e.g.* Bohrer and Schultze, 2008).

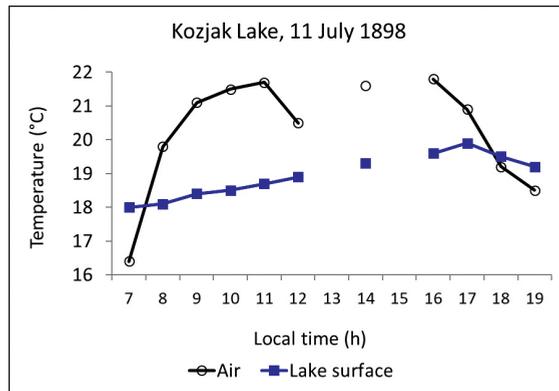


Figure 22. Diurnal variation in the air and the lake surface temperature for Lake 12 on 11 July 1898 (according to data provided by Gavazzi, 1919). The minimum and maximum air temperatures were 9.7 °C (the night of 10/11 July) and 22.9 °C (approximately 15:30 local time), respectively.

which was due to the higher specific heat capacity of the water relative to the air.

Stratification is one of the key phenomena in lakes (*e.g.*, Boehrer and Schulze, 2008). Gavazzi (1919) was the first to publish his observations on stratifications in the Plitvice Lakes (Fig. 23). He pointed to the fact that, during the summer, all lakes had surface temperatures substantially above 4 °C; furthermore, at some depth, there was a transition layer characterized by rapid temperature changes (*i.e.*, metalimnion⁴¹ or thermocline⁴²), which divided the upper, relatively warm layers from the lower, colder layers. The author remarked that this transition layer can occasionally be only several decimeters or even several centimeters deep; additionally, it was always found in the Plitvice Lakes during summertime.

Based on the conclusions of, at that time, the state-of-the study of Merz⁴³, Gavazzi elaborated reasons for the establishment of the thermocline. Namely,

⁴¹ In the summertime, there are three layers in the lake that are distinguished based on the typical vertical temperature profile: epilimnion (upper portion of the lake under the seasonal air temperature influence); metalimnion or thermocline (the layer between the upper and lower lake portions); and hypolimnion (the lower lake portion). Gavazzi (1919) did not specifically use the term metalimnion (thermocline). Instead, he called this layer the transition layer, and he mentioned its French (*couche critique*) and German (*Sprungschichte*) names.

⁴² Some authors distinguish between the metalimnion and thermocline. Hutter et al. (2011), for example, define the metalimnion as a layer separating the epilimnion from the hypolimnion, while the thermocline is the surface within the metalimnion at which the absolute value of the vertical temperature gradient is maximal. As did Kalff (2002), in the present review, we use the terms metalimnion and thermocline as synonyms.

⁴³ Merz, A. (1911): *Die Sprungschichte der Seen. Mitteilungen des Vereind d. Geographen a. d. Universität Leipzig.*

mechanical convection, which is generated by waves (and is, thus, more efficient for higher waves and shallower depths), mixes the lake water up to a certain depth. In other words, warmer water parcels are transported to greater depths, and conversely, cooler parcels are transported toward the lake surface. This results in the establishment of homothermal layer. (Across this layer, both the temperature and the specific weight are constant.) Consequently, during the summertime events dominated by mechanical convection, the temperature of the surface water decreases while the temperature of deeper layers increases with respect to their initial states.

Apart from mechanical convection, thermal convection also occurs in a lake. During the nighttime (and during the fall and winter), the water at the surface gradually cools and becomes denser. Once the specific weight of the surface parcels becomes greater than the specific weight of the parcels below, the surface parcels sink and mix with the parcels found below. Thus, due to the mixing, all parcels found below will eventually attain both an average specific weight and an average temperature. During the fall, when the surface water starts to cool as early as in the daytime, the depth of the layer in which thermal convection occurs increases. Accordingly, the depth of the transition layer is reduced from above, and the vertical temperature gradient decreases. Gavazzi (1919) assumed that the transition layer (*i.e.*, the metalimnion) was composed of a large number of very thin layers. Due to thermal convection, these thin layers gradually cool, and cooling first starts at the uppermost layer. Thus, the layers that initially belonged to the transition layer become a part of the upper, homothermal (isothermal) layer. Therefore, the transition layer becomes thinner, and its upper border shifts downward towards greater depths. By the end of fall, when the water at the surface that has been gradually cooling reaches a temperature equal to that of the lower border of the transition layer, the transition layer disappears. Thus, due to thermal convection, the homothermal layer spreads from the surface towards greater depths and can eventually reach the bottom of a lake.

Finally, Gavazzi (1919) summarized the following a) if a lake's surface temperature is above 4 °C, mechanical convection results in the cooling and warming of the upper and lower lake layers, respectively. Conversely, if a lake's surface temperature is below 4 °C, the result is opposite. That is, the upper layers warm, while the lower layers cool; and b) if a lake's surface temperature decreases down to 4 °C, thermal convection results in the cooling of the lower lake layers. In contrast, if the lake's surface temperature increases from 0 °C to 4 °C, thermal convection results in the warming of the lower lake layers.

Gavazzi (1919) also reported on the occurrence of multiple transition layers. He showed two cases in which three transition layers were found in the lower portion of Lake 12 (Fig. 23c): on 23 July 1897, these were found at depths of 8.25 m, 12.5 m and 16.5 m, respectively, while the next day they were at depths of 7.55 m, 13.5 m and 16.5 m. The author associated the occurrence of multiple transition layers with mechanical convection. Namely, if mechanical convection

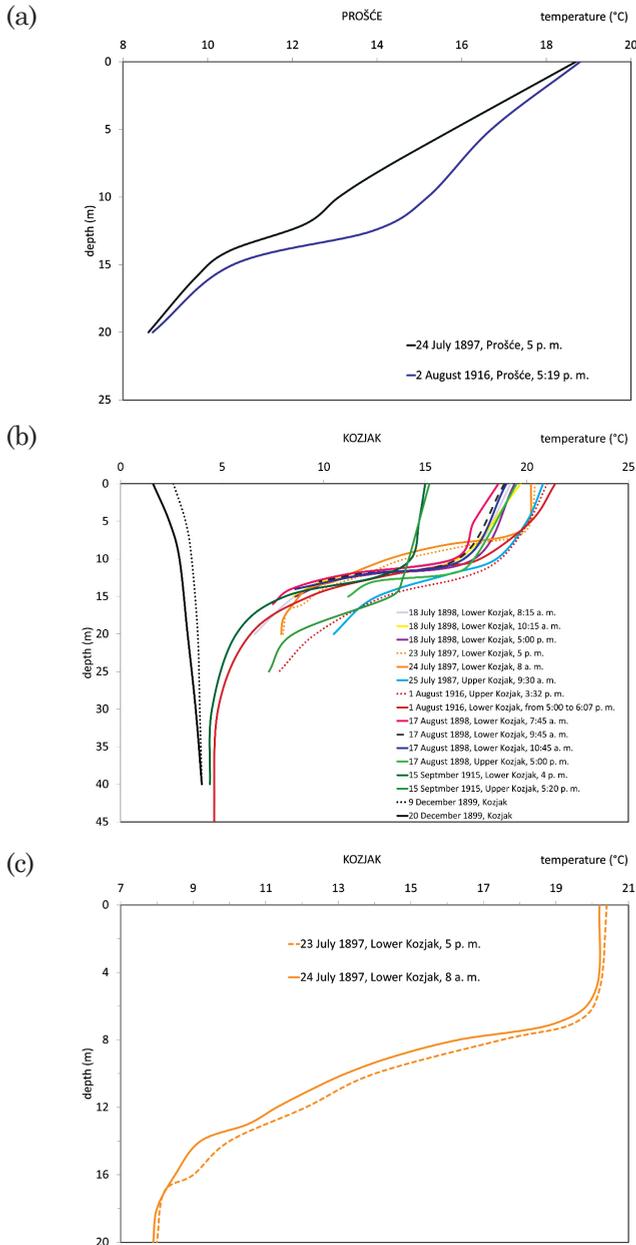


Figure 23. The first published temperature measurements depicting stratifications of Lake 1 (a) and Lake 12 (b) (Gavazzi, 1919). Most frequently, but not always, Gavazzi distinguished between the upper and lower portions of Lake 12. Similarly, most frequently, but not always, he reported his observation times. Panel (c) shows an enlarged view of the two cases with multiple transition layers in lower (northern) portion of Lake 12.

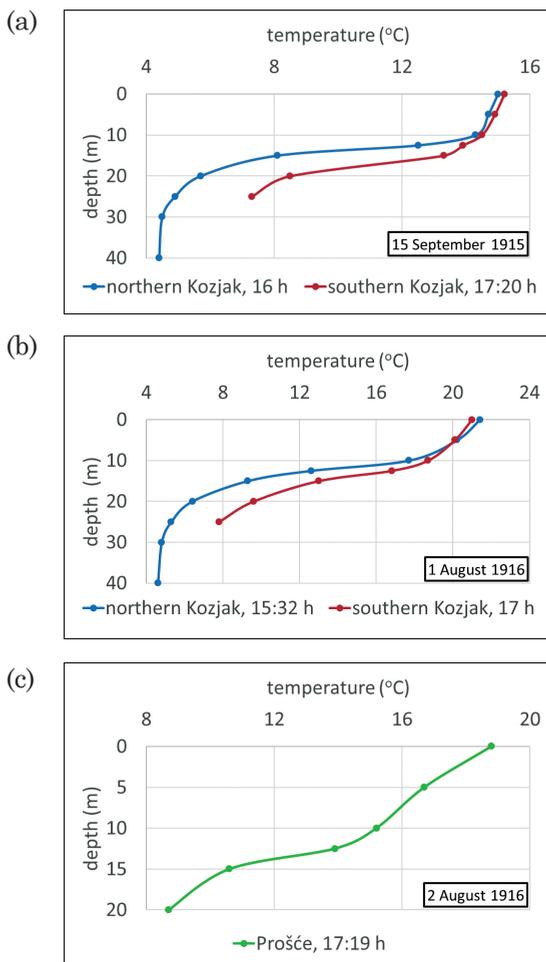


Figure 24. Stratifications of southern (upper) and northern (lower) parts of Lake 12 on 15 September 1915 (a), and 1 August 1916 (b). Panel (c) shows stratification of Lake 1 on 2 August 1916. Data are taken from Gavazzi (1919).

develops several times consecutively, but has a weaker intensity each time, the deepest transition layer will be associated with the first (strongest) event of mechanical convection, and the next shallower transition layer will be produced by successive, less intense event of mechanical convection, and so on.

For approximately the first 5 m of Lake 12, there is no difference between the temperatures observed at the upper (southern) and the lower (northern) portions of the lake. However, at larger depths, the difference emerges (Fig. 24, panels a and b). Gavazzi (1919) argued that the temperature differences arise due to a submerged barrier that stretches from the lake bottom up to approxi-

mately 5 m below the lake's surface (see Figs. 1 or 2, Section 2). Thus, at depths greater than 5 m, Lake 12 is composed of two separate basins, which exhibit different temperature patterns.

At greater depths (> 12 m), temperatures in Lake 1 are higher than the temperatures in northern part of the Lake 12 at the same depth (Fig. 24), although the altitude of Lake 1 is approximately 102 m higher than the altitude of Lake 12. Gavazzi (1919) argues that this is due to the influence of tributaries Matica (Lake 1) and Rječica (southern part of Lake 12), which receive large quantities of suspended matter during snowmelt and/or intense precipitation. Tributary water, which is rich in suspended matter, has a higher density (and higher turbidity) than the lake water. However, its temperature is only slightly lower than the temperature of water at the lake surface, but it is noticeably higher than the temperature of the deeper lake layers. Therefore, denser and more turbid tributary water penetrates deeper into the lake (occasionally, even down to the lake bottom) and thus, causes an increase in temperature in the deep lake layers. Such "hydrostatic convection" occurs only in lower layers of Lake 1 and southern part of Lake 12, which receive sediment-rich water. In northern part of Lake 12 there is no such process, or it is very weak due to the submerged barrier. Namely, the transport of water across the submerged barrier from the southern to the northern part of the lake occurs only in the first ≈ 5 m of the lake, and these layers contain a small fraction of the turbid, warm, sediment-rich water. As a result, the deep layers of Lake 1 and southern part of Lake 12 are warmer than the layers of the same depth in northern part of Lake 12.

Petrik (1958, 1961) also investigated the water temperatures of the Plitvice Lakes. During several years, he measured the surface temperatures of the sources, brooks, channels, waterfalls and lakes at several measuring sites. The author concluded that during the warm part of the year (*i.e.*, from May to September) the range of watercourse source temperatures was from 7.2 to 12.5 °C. During the warm part of a year, apart from the *Crna rijeka* source, the sources of watercourses that inflow into Lake 1 have mean temperatures that approximately correspond to the annual mean air temperature of the area. However, the temperatures of main sources of *Crna rijeka* and Plitvica Brook are higher and lower, respectively, than the annual mean air temperature. Petrik attributes the colder water of Plitvica Brook to the fact that, in comparison with other watercourses, Plitvica is fed by the water that originates from higher altitudes (Mala Kapela mountain chain). Petrik also found that the surface water temperatures of brooks increase downstream. Similar results were found for the surface temperatures of Lake 1 during the summertime. For example, for the measurement performed on 12 September 1952 between 09:47 and 10:28 h local time, the surface temperatures increased northward, from 16.2 °C to 16.9 °C. Conversely, the surface temperatures of Lake 12 that were measured on 9 and 10 of September (both between 15:00 and 17:30 local time) did not exhibit such behavior; rather they were uniform.

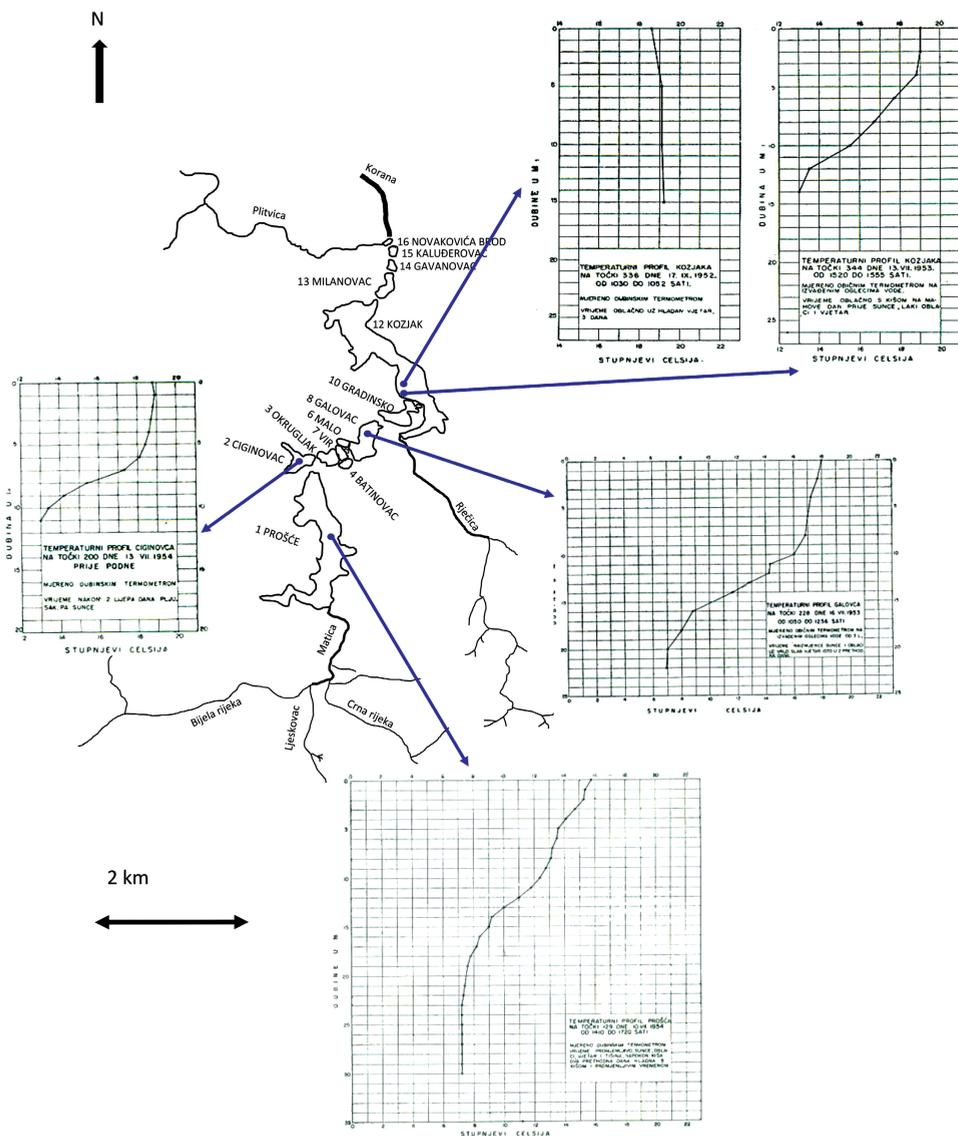


Figure 25. Composite picture of the original vertical profiles of water temperature (Petrik, 1958) for Lake 1 on 10 July 1954, Lake 2 on 13 July 1954, Lake 8 on 16 July 1953 and Lake 12 on 17 September 1952 and 13 July 1953 (left and right profile, respectively). Full blue circles (starting points of blue arrow lines) indicate the positions of the measuring sites. The horizontal and vertical axes show temperature (°C) and depth (m), respectively.

Apart from the surface temperatures, Petrik (1958) also measured the temperatures at various lake depths. Figure 25 illustrates few examples of vertical

profiles. Based on multiyear summertime observations, the author concluded the following:

- The stratification of lakes is a slow process. Lakes reach full stratification only at the end of summer, *i.e.*, in September. As summer progresses, the upper boundary of the thermocline descends to greater depths.

- The stratification of Lake 1 is governed by the temperature of *Crna rijeka*. During the summertime, the hypolimnion temperature of Lake 1 is 2–3 °C higher than +4 °C due to the inflow of relatively warm water from *Crna rijeka*. Therefore, the thermocline in Lake 1 is not very prominent (because the temperature gradient along the thermocline is low). Accordingly, stratification of the southern, upstream part of Lake 1 is weak (even in regions of greater depths), while it strengthens downstream. In the downstream, northern part of the lake, the depth of the epilimnion is small (2–4 m), while the temperatures are between 15 and 18 °C. The hypolimnion appears at a depth of approximately 20 m, and its temperature is between 6 and 8 °C. Finally, the temperature range of the thermocline is 7–11 °C.

- Lake 1 freezes later than Lake 12, although its altitude is ≈ 100 m higher. Again, this is due to the influence of *Crna rijeka*, *i.e.*, due to the inflow of relatively warm water from *Crna rijeka*.

- The temperatures of the hypolimnia of Lake 2 (Ciginovac), Lake 3 (Okrugljak), Lake 6 (Malo), Lake 7 (Vir) and Lake 4 (Batinovac), Lake 8 (Galovac) and Lake 10 (Gradinsko)⁴⁴, which receive water from Lake 1, are elevated since these lakes always receive warmer water due to the influence of *Crna rijeka*.

- Lake 2 and and Lake 8 are sheltered from winds and are, therefore, calm. Thus, they stratify both faster and stronger, and they reach full stratification.

- The stratification of Lake 12 is mainly governed by morphological factors, *i.e.*, low depth of the upstream, southern part of the lake; accelerated flow in channels along the lake island; and a submerged barrier. Therefore, upstream of the submerged barrier, Petrik did not observe full stratification, although he hypothesized that full stratification might be established at the end of summer. In channels along the island, the author observed different patterns of stratification: an isothermal (homothermal) profile, a uniform drop in temperature with depth, or several shallow thermal layers. In the downstream, northern portion of Lake 12 where depths are the greatest, the top of the thermocline was observed at depths between 4 and 10 m. The temperatures of the epilimnion were between 12 and 22 °C, while the temperature in the thermocline was between 14 and 15 °C. The top of the hypolimnion was observed at depths between 14 and 24 m, and its temperature was slightly above +4 °C.

⁴⁴Petrik (1958) referred to the lakes 2, 3, 4, 6, 7, 8 and 10 as the Middle Lakes. In addition, for the lakes 6 and 4 he used the names Jovinovac and Bakinovac, respectively.

• The lakes 13–16 (*i.e.*, Milanovac, Gavranovac, Kaluđerovac and Novakovića Brod, respectively ⁴⁵) are homothermal (isothermal) during the summertime. This is because these lakes receive water solely from the epilimnion of Lake 12.

In a later investigation, Petrik (1961) addressed the lake temperatures. During 1955, 1958, 1959 and 1960, he performed over 2000 measurements, and he compared the obtained results with the results of a previous study (Petrik, 1958). For example, he noted that the summertime temperature range for the main source of *Bijela rijeka* increased from 7.6–7.8 °C (older dataset) to 7.1–8.2 °C (newer dataset). Similarly, the temperature range for the main source of *Crna rijeka* increased from 8.0–8.4 °C (older dataset) to 7.6–8.2 °C (newer dataset). The author also discussed the heating of the surface water downstream from the main sources towards Sastavci (Fig. 26), which was observed during the warm season. This heating was most prominent downstream from sources, towards the exit from Lake 1, and it was particularly notable along Lake 1; in contrast, less heating occurred in Lake 12. Furthermore, in Lake 1, the temperature increased at both the surface and in the deeper layers. The highest observed summertime heating along the entire water system was approximately 13 °C. During the cold part of the year, the surface water cooled downstream.

In the same investigation, Petrik (1961) again determined the vertical temperature profiles, and he supplemented the results with profiles for Lake 3 (Okrugljak), Lake 7 (Vir), Lake 11 (Burgeti⁴⁶) and Lake 10 (Gradinsko). For the summertime vertical profiles, he obtained results similar to those of the previous study (Petrik, 1958). After comparing the vertically averaged water temperatures for all lakes, he concluded that, apart from lakes 13–16, the vertically averaged temperature decreased with the lake depth. In other words, the vertically averaged water temperature of the particular lake decreased downstream since the lake depth increased downstream (see Section 2). Small, shallow lakes were not stratified. Instead, they were roughly homothermal (isothermal). The more downstream the lake was, the more pronounced its isothermal pattern was.

For Plitvice Lakes, which are exorheic⁴⁷, the equation of heat balance is as follows (Petrik, 1961):

$$T_u - T_i + T_j - T_e = T_a, \quad (13)$$

where T_u is a heat that is brought to a lake by inflow. It depends on the inflow of water into the lake and on the temperature of the water. For example, Lake 1 receives colder water relative to other downstream lakes during the summertime, while Lake 12, due to the inflow from Rječica, receives the largest quantity of water. T_i is the heat that is taken from the lake due to outflow. The value depends on the outflow from the lake and on the temperature of the water that

⁴⁵ Petrik (1958) refers to these lakes as the Lower Lakes.

⁴⁶ Petrik (1958, 1961) used the name Veliki Burget.

⁴⁷ Exorheic or open-basin lakes are lakes that have water inflow and outflow; thus, they are freshwater lakes. Conversely, endorheic or closed-basin lakes do not have water outflow (*e.g.*, Kalff, 2002).

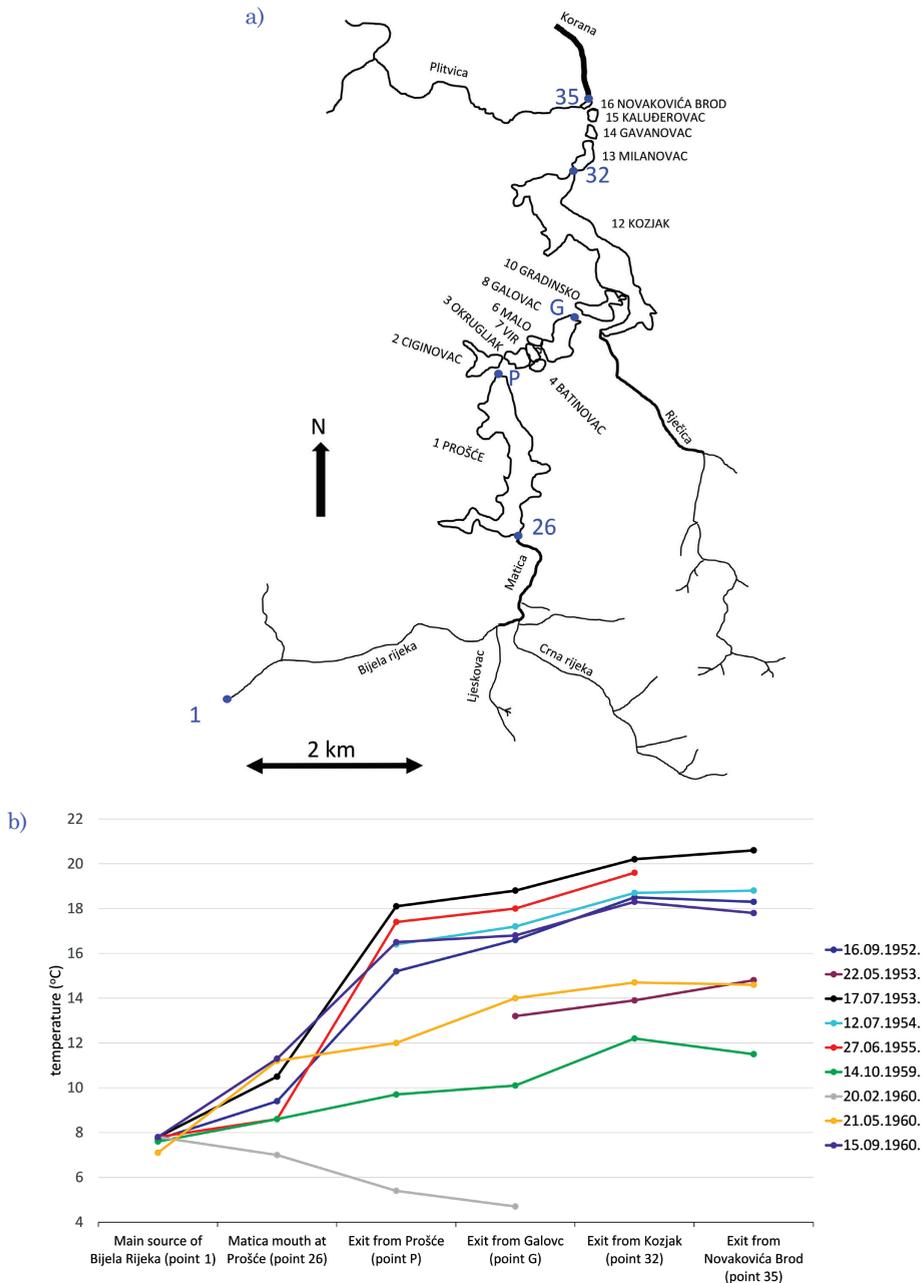


Figure 26. Position of measuring sites of surface water temperature (a) and downstream profile of the surface water temperature for different days, as observed by Petrik (1961) (b). Days of observations are listed in the format DD.MM.YYYY. (legend in panel b). Except for wintertime measurement (20 February 1960), surface water temperature always increased downstream.

flows out. T_j is the net heat received within the lake basin due to conduction, convection and radiation (*i.e.*, the net difference between the gains and losses within the lake due to heat conduction, convection and radiation). This term is more important for larger than for smaller lakes. T_e is the difference between the heat losses due to evaporation and the heat gains due to condensation of water vapor at the lake surface. This term increases with the area of the lake surface, and it depends on the lake's altitude and exposure to winds. Finally, T_a is the heat accumulated within the lake. It can be positive or negative, depending on the eventual gain or loss of net heat. It differs from lake to lake.

Based on the observed vertical profiles of lake temperature, Petrik (1961) calculated the heat accumulated in the vertical water column (T_a) during investigated time interval. The height of the water column corresponds to the lake depth, while its base has an area of 1 cm^2 . The author estimated the heat that accumulated in the water column during the period, which started with establishment of the springtime homothermal conditions at the temperature of $+4 \text{ }^\circ\text{C}$ and ended with the achievement of the maximum water column temperatures in late summer/early fall. For the water column located in the northern portion of Lake 12 (point 358 in Fig. 27), he obtained a value of $101.398 \text{ kJ cm}^{-2}$, where

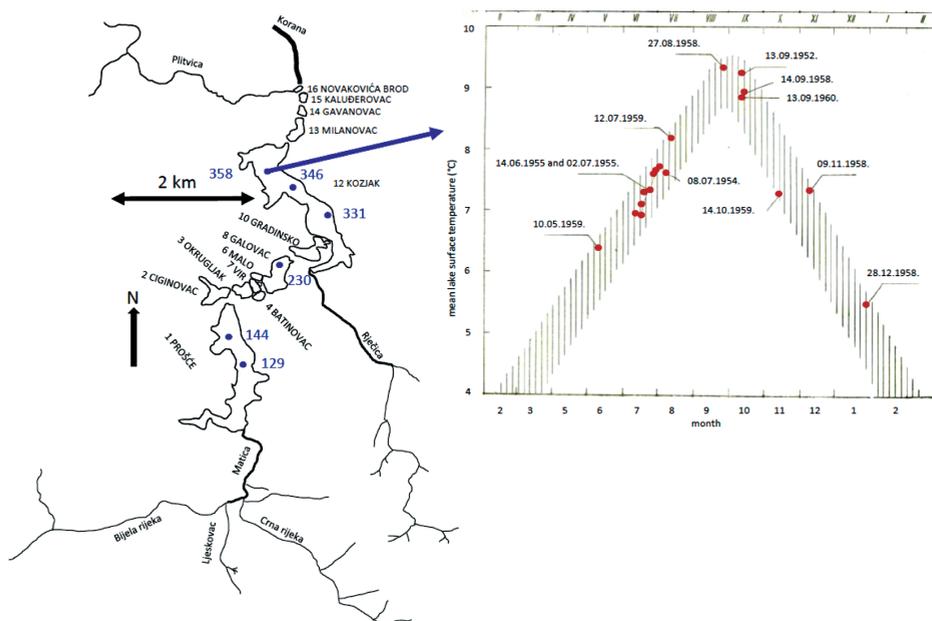


Figure 27. *Left:* Positions of points for which Petrik (1961) calculated the heat that accumulated in the water column (Tab. 10). Points are indicated by blue full circles and corresponding numbers. *Right:* Annual variation in lake surface temperature determined by Petrik (1961) for the point 358 in northern part of Lake 12. Full red circles show individual measurements. Dates of some measurements are indicated in the format DD.MM.YYYY.

Table 10. Heat (T_a in Eq. 13) accumulated in the water column during the period starting at spring-time homothermal conditions (i.e., mean temperature of water column = +4 °C) and ending at the date of measurement, as calculated by Petrik (1961). Positions of points (water columns) are depicted in Fig. 27. Each water column has a base of 1 cm², while its height corresponds to the lake depth.

Point	Measurement date (DD.MM.YYYY.)	Mean temperature of water column (°C)	Lake depth (m)	T_a (kJ cm ⁻²)
129	29.06.1955.	10.681	28	78.353
129	03.07.1955.	11.117	28	83.381
144	29.06.1955.	9.746	36	86.733
144	03.07.1955.	10.182	36	93.437
230	04.07.1955.	12.190	22	75.420
331	28.06.1955.	13.608	20	80.448
331	02.07.1955.	13.975	20	83.800
346	28.06.1955.	12.131	24	81.705
346	02.07.1955.	12.646	24	87.152
358	28.06.1955.	7.584	44	66.202
358	03.07.1955.	7.717	44	68.716

he assumed⁴⁸ the maximum mean water column temperature was 9.5 °C. For the same location, the author determined the annual variation in the surface water temperature (Fig. 27). Finally, for several points Petrik calculated the heat (T_a) that accumulated in the water column during the period from springtime homothermal conditions (+4 °C) to the date of measurement (Tab. 10).

Unfortunately, there is still no measuring site that includes a long-term time series of water temperatures in the PLA. However, in recent years, various authors have occasionally observed and/or analyzed available lake temperatures data (e.g., Babinka, 2007; Biondić et al., 2008; Barešić, 2009; MARIE CURIE ACTIONS - IRSES PROJECT STRAVAL, 2010; Vurnek et al., 2010; Sironić et al., 2017). For example, Babinka (2007) argued that Lake 1 and Lake 12 are stratified during the summer, while they are mixed during spring and fall. Generally, during the winter, there is no wind-forced mixing because the lake surfaces are frozen. Additionally, for September 2004, she found thermoclines at depths of 10–15 m (Lake 1) and 15–18 m (Lake 12). Furthermore, a comparison of older and newer data clearly showed that the average and maximum water temperatures in recent years were noticeably higher than those from a few decades ago (Barešić, 2009; Sironić et al., 2017). Thus, Barešić (2009) found that the surface water temperatures observed for Lake 1, Lake 11, Lake 12 (location Most) and Lake 16 during the period of 2003–2007 were approximately 1–2 °C higher than those observed at the same places *ca.* 20 years ago. On the other hand, the surface temperatures of the watercourse sources remained

⁴⁸ Petrik (1961) measured the vertical temperature profile of the water column at point 358 (Fig. 27) on 13 September 1952, and for this day, he obtained a vertically averaged temperature of 9.242 °C. Since he did not measure water temperatures every day, in the calculation, he assumed a slightly higher maximum mean temperature (9.5 °C).

unchanged. Similarly, Sironić et al. (2017) also found an increase in the mean surface temperatures for lakes (1.5 °C) and springs of *Bijela rijeka* (0.6 °C) and *Crna rijeka* (0.4 °C) over approximately last three decades, as already discussed in Section 5.

Water flow

Petrik (1958) investigated the flow of water through lake system. He emphasized that lakes receive water mainly from *Crna rijeka*, *Bijela rijeka* and their tributaries, as well as from Rječica and its tributaries. During the summer, from the southern part of Lake 1 to Lake 12 there is almost no water inflow. Thus, all changes that occur in this part of the lake system are result from the physical, chemical and biological processes occurring inside the lakes themselves. However, this is not true for the downstream part of the system (as of Lake 12), since Lake 12 receives substantial quantity of water from the Rječica River. The influence of Rječica is clearly seen in the change in alkalinity (see footnote 12) in Lake 12 relative to the upstream lakes. Furthermore, water flows from upstream lakes to downstream lakes only in shallow rapids across waterfalls and cascades. Therefore, once summertime stratification has been achieved, only the water from the uppermost, epilimnion layer of an upstream lake overflows to a downstream lake. (Water from greater depths is denser and thus, cannot reach the top of the barrier.) Accordingly, during summertime, the thermal, chemical and biological characteristics of the downstream lake depend on the characteristics present in the epilimnion of the upstream lake. (Conversely, water that is in the thermocline and hypolimnion of the upstream lake cannot substantially affect the characteristics of water in the downstream lake.) Therefore, the summertime flow of water through the lakes is much faster than expected from the lake volumes alone. In other words, water flows only through the epilimnion; however, water at greater depths is stagnant or moves within the lake itself. Petrik corroborated this assertion using a water-dye experiment⁴⁹, which he performed in Lake 14 (Gavanovac). The author selected Lake 14 due to its morphometry (this lake is not too large or too deep, and it has a relatively simple shape). Based on the temporal change in the concentration of dye in the lake, Petrik estimated that during the experiment, the water discharged from Lake 14 was approximately 600 l s⁻¹. From the same data, Petrik determined the dispersion index (*DI*), which is defined as a ratio:

$$DI = t_{90} / t_{10}, \quad (14)$$

where t_{90} and t_{10} are the time intervals needed for 90% and 10% of water (*i.e.*, 90% and 10% of the dye injected into lake) to run out of the lake, respectively (*e.g.*, Teixeira and Siqueira, 2008). He obtained $t_{90} = 1775.4$ min (≈ 29.6 hours),

⁴⁹ On 16 August 1951, Petrik injected an alkaline solution of uranine (750 g of uranine and 200 g of alkali) at the top of the main central waterfall and followed the spread of dye. (Uranine C₂₀H₁₀Na₂O₅ is disodium salt of fluorescein C₂₀H₁₂O₅. It is a yellow-green dye that is frequently used as a tracer.)

t_{10} = 41.53 min, and DI = 42.75. Based on the obtained high value of the dispersion index, Petrik concluded that water (in epilimnion) flows quickly through Lake 14.

Petrik (1958) discussed lake water losses into the underground, as well as underground inflows from lake to lake. He also quoted data from older sources that stated that measured outflows from Lake 1 and Lake 15 were 1043 l s^{-1} and 894 l s^{-1} , respectively, while the water discharge at the upper portion of the Korana River was 1262 l s^{-1} . However, the author emphasized that there was no information explaining whether these data had been derived from individual or multiple measurements, nor did they correspond to simultaneous measurements or had been observed at different times. Additionally, based on his measurements, Petrik concluded that Lake 2 (Ciginovac) loses water through underground flow; moreover, in July 1953, this loss was approximately 30 l s^{-1} .

Biological and hydrogeochemical studies also report occasional observations related to the water velocity in the PLA. Pavletić (1957), for example, stated that in June, the water velocity at waterfalls varied between 0.5 and 3 m s^{-1} , while at one location in the Labudovac Channel, he measured a value as high as 4 m s^{-1} .

Waves

In the early limnological study of Plitvice Lakes, Gavazzi (1919) also addressed lake waves. The author discussed surface *vs.* internal waves, as well as progressive *vs.* standing waves. He emphasized that the progressive waves (both surface and internal) resulted in homothermal conditions, which were found down to a certain lake depth. On the other hand, standing internal waves (internal seiches) did not produce homothermal layers since the water parcels do not mix. Instead, water parcels move along same path while vertically moving up and down. Accordingly, isothermal surfaces also move up and down. In this early discussion of lake waves, Gavazzi did not distinguish properly between the short waves and the long waves and he did not allow for the velocity shear when interpreting the turbulence. This is not surprising since Lewis Fry Richardson defined the parameter (Richardson number), which takes into account the velocity shear and which is useful for distinguishing between the turbulent and non-turbulent flows in 1920 (Richardson, 1920). Today, it is known that the mixing is strongly supported by the short waves and long baroclinic waves (due to the strong velocity shear); in contrast, the mixing is weakly supported by long barotropic waves (due to the weak velocity shear). Other wave properties (*e.g.*, progressive *vs.* standing) are of secondary importance for the mixing of fluid.

a) Standing surface waves (surface seiches)

In lakes, surface seiches⁵⁰ are mainly caused by variable winds (*e.g.*, Kalff, 2002). The water at one end of the lake rises in response to a steady wind from

⁵⁰Surface seiches are long-periodic, non-dispersive free oscillations occurring in enclosed or partially enclosed bodies of water, such as lakes, channels, estuaries, bays, harbors and marginal seas. Generally, they can be generated by variable winds, atmospheric pressure disturbances,

the opposite direction. When the wind becomes weaker, the water flows back in the opposite direction. While flowing back, it overshoots the equilibrium position and starts to oscillate in the vertical direction as a standing wave, which rocks back and forth. The simplest type of surface seiche is uninodal⁵¹. Such seiches are characterized by a maximum vertical transport at the two antinodes and none at the node. On the other hand, horizontal transport in the case of uninodal surface seiches is greatest at the nodes, where the velocity of horizontal transport is a direct function of seiches' amplitude. In moderate-sized lakes, surface seiches have a typical vertical amplitude of a few centimeters; thus, they are of little interest in biological and chemical limnology. Periods of uninodal surface seiches are lake specific and vary from minutes to several hours, for small and great lakes, respectively.

While the first worldwide report of surface seiches was reported by François Alphonse Forel⁵² for Lake Geneva in 1873 (Vincent and Bertola, 2012), the results of the first investigations of uninodal standing surface waves for the Plitvice Lakes were first published in 1919 (Gavazzi, 1919). Since Gavazzi did not have the necessary equipment to record surface seiches⁵³, he calculated periods of uninodal seiches from Merian's formula⁵⁴:

$$T = 2L(gd_s)^{-1/2}, \quad (15)$$

where T is the seiche period (s), L is the length of the lake/basin (m), g is the acceleration due to gravity (9.81 m s^{-2}) and d_s is the mean depth of the presumed rectangular lake/basin (m).

Since Merian's formula is valid for rectangular lakes, Gavazzi applied Defant's method (Defant, 1918) to check whether the formula could be applied to a lake with an irregular shape. (Gavazzi even exchanged written correspondence with Defant to obtain additional explanations regarding that, at that time, novel method.) Defant's method required determination of three quantities, *i.e.*, q , 2ξ , and $2\Delta\eta$ (*i.e.*, 2η):

strong rainfall, tides and tsunamis. Seiches are standing waves. Therefore, they can be considered as a sum of two progressive waves of the same wavelength travelling in opposite directions. The frequency of oscillations depends on the size of the basin and its bathymetry. Basic equations of surface seiches are provided in Appendix I.

⁵¹ However, interactions between uninodal seiches and lake morphometry or intensive rain on a lake center can establish multinodal seiches (Kalff, 2002).

⁵² Forel is a founding father of limnology. In 1892, he explained that research interests associated with lakes are too large to be classified within any existing integrative discipline, and thus, he was forced to create a new word (limnology) for a new discipline; further he explained, '*limnology is thus the oceanography of lakes*' (Vincent and Bertola, 2012).

⁵³ Conventionally, surface seiches can be recorded using a water level recording device, *i.e.*, limnograph.

⁵⁴ Derivation of Merian's formula for multinodal period is provided in Appendix II.

$$\begin{aligned}
 q_i &= 2 \eta_{i-1} v_i, \\
 2\xi_i &= -(q_i + q_{i-1}) / s_i, \\
 2\Delta\eta_i &= 4 \pi^2 \cdot 2 \xi_i \Delta u_i / (g T^2),
 \end{aligned}
 \tag{16}$$

where $i = 1, 2, 3, \dots, n$; n is the number of a lake's vertical cross-sections, Δu_i is the distance of the i^{th} lake cross-section from the preceding $(i-1)^{\text{th}}$ cross-section (m), v_i is the lake surface area of the i^{th} section (m^2), and s_i is the surface of the i^{th} vertical cross-section (m^2) (Fig. 28). The water levels at the starting and ending edges of the lake are $2\eta_0$ and $2\eta_n$, respectively, while $2\eta_i$ is the water level at the i^{th} section (cm). The difference in the water levels between the two adjacent cross-sections is $2\Delta\eta_i = 2\eta_i - 2\eta_{i-1}$ (cm), while q_i is the volume of water that passes through the i^{th} cross-section (m^3). Gavazzi assumed that the last (n^{th}) cross-section corresponded to the ending edge of the lake. Accordingly, he argued that if the water volume that passes through the last vertical cross-section equals zero, ($q_n = 0$), then the period of oscillations T (s), which is determined using Merian's formula (15), is appropriate, and, consequently, the position of the uninodal line calculated based on this period is correct. However, the author rarely obtained an exact value of $q_n = 0$. Instead, the calculated q_n values were slightly above or below zero. Therefore, he used a graphical method to determine the appropriate period. Specifically, if q_n was above zero, he decreased the value

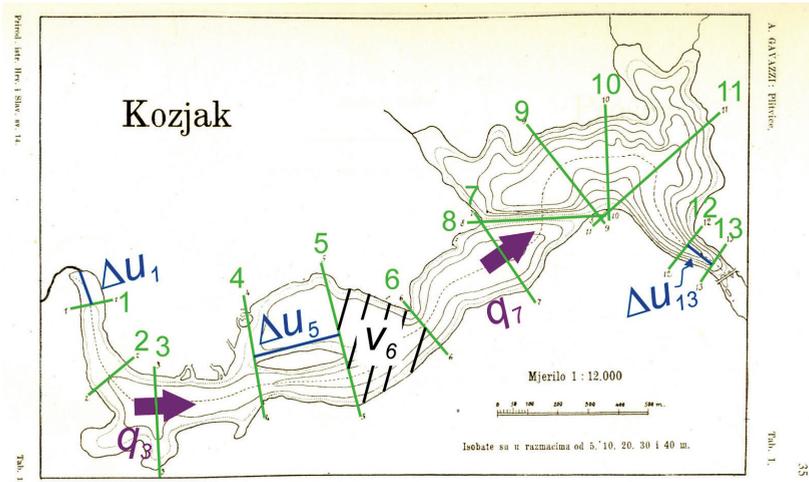


Figure 28. Illustration of Gavazzi's (1919) application of Defant's method (Eqs. 16) to Lake 12. Positions of 13 vertical cross-sections ($i = 1, 2, \dots, 13$), as selected by Gavazzi, are shown in green. (Note that Gavazzi took the last (13th) cross-section as the ending edge of the lake.) Distances between the i^{th} and $(i-1)^{\text{th}}$ cross-sections (Δu_i), the water volumes passing through the i^{th} cross-sections (q_i), and the lake surface areas defined by the two adjacent cross-sections (v_i) are depicted in blue, purple and black, respectively. Lake borders and isobaths of 5, 10, 20, 30 and 40 m (brown) are copied from Gavazzi's paper.

of the period T in order to obtain $q_n < 0$, and vice versa; if the volume of q_n was below zero, he increased the value of period T to obtain $q_n > 0$. Thereafter, he drew a graph with the two volume values (*i.e.*, one positive and one negative) at abscissa, while at the ordinate, he positioned the corresponding periods. The line that connected the two (q_n, T) points, intersected the ordinate at the required period T (*i.e.*, at the period that corresponded to the value $q_n = 0$).

After applying Merian's formula (Eq. 15) to Lake 1, where $L = 2830$ m, $g = 9.8$ m s⁻² and $d_s = 13.2$ m, Gavazzi obtained a period of $T = 498$ s; when using Defant's method, he obtained a somewhat smaller value of $T = 458$ s (Tab. 11). The author concluded that the reasonably good agreement between the two methods was due to the relatively simple bathymetry of Lake 1. However, for Lake 12, where $L = 3095$ m, $d_s = 17.3$ m, and the total lake surface area was 0.8244 km², the discrepancy between the results of the Merian's and Defant's methods was noticeably larger. While Merian's formula gave a $T = 476$ s, the

Table 11. Periods of surface seiches lakes 1 and 12 obtained by different methods. The data were observed at two measuring sites for each lake.

Lake 1 P R O Š Ć E					
Reference	Bathymetry	Method	Mode	Period (s)	Comment
Gavazzi (1919)	Gavazzi (1919)	Merian's formula (Eq. 15)	1 st	498	
		Defant's method (Eqs. 16)	1 st	458	
	N/A	Observed	1 st	510	
2 nd			300		
3 rd			198		
4 th			162, 150	Both peaks in the power spectrum are non-significant.	
5 th			132		
Pasarić and Slaviček (2016)	L = 2927 m d _s = 10.7 m	Merian's formula (Eq. 15)	1 st	570	
			2 nd	288	
			3 rd	192	
			4 th	144	
			5 th	114	
Gavazzi (1919)		Modified Defant's method	1 st	438	
			2 nd	270	
			3 rd	162	
			4 th	120	
			5 th	114	
Petrik (1958)		Modified Defant's method	1 st	576	
			2 nd	330	
			3 rd	210	
			4 th	162	
			5 th	132	

Table 11. Continued.

Lake 12 K O Z J A K					
Reference	Bathymetry	Method	Mode	Period (s)	Comment
Gavazzi (1919)	Gavazzi (1919)	Merian's formula (Eq. 15)	1 st	476	
		Defant's method (Eqs. 16)	1 st	565	
	N/A	Observed	1 st	540	
			2 nd	294	
			3 rd	216, 186	Both peaks in the power spectrum are non-significant.
4 th	156				
5 th	138 / 126*	*The period of 126 s is the most probably result of aliasing. Authors argue that correct period is 114 s.			
Pasarić and Slaviček (2016)	L = 3066 m d _s = 13.2 m	Merian's formula (Eq. 15)	1 st	540	
			2 nd	270	
			3 rd	180	
			4 th	132	
			5 th	108	
	Gavazzi (1919)	Modified Defant's method	1 st	516	
			2 nd	294	
			3 rd	198	
			4 th	156	
			5 th	108	
	Petrik (1958)	Modified Defant's method	1 st	540	
			2 nd	306	
			3 rd	204	
			4 th	156	
			5 th	114	
Petrik (1958)	Modified Defant's method	1 st	144	Deeper (northern) sub-basin.	

application of Defant's method resulted in a $T = 565$ s. Gavazzi concluded that this result was due to very complex bathymetry of Lake 12, including one island and underwater barrier that divides the lake basin in two sub-basins (Fig. 2). Therefore, he hypothesized that Lake 12 might have three uninodal lines, *i.e.*, one corresponding to the entire lake and the other two corresponding to the upper (southern) and lower (northern) portion of the lake, respectively.

Almost 100 years later, Pasarić and Slaviček (2016) recalculated the periods of surface seiches for lakes 1 and 12 using Merian's method and a modified Defant's method (Orlić, 2010). The authors used two different historical bathymetries: one provided by Gavazzi (1919) and the other by Petrik (1958). While Gavazzi (1919) calculated periods solely for uninodal waves, Pasarić and Slaviček addressed higher modes as well. Furthermore, due to the complex shape of the Lake 12 basin, they also distinguished between the two sub-basins: the deeper

(northern) and the shallower (southern) sub-basins. Additionally, based on a campaign of special 1-min instantaneous water-level measurements performed at four measuring sites (two per lake) in 2008, Pasarić and Slaviček also reported on empirical modes, which were determined from power spectra (Tab. 11). Although the bathymetry of Lake 12 is far more complex than that of Lake 1, for both historical bathymetries, they found much better agreement between the observed and the calculated periods for Lake 12 than for Lake 1. In addition, the results obtained with the two historical bathymetries differed more for Lake 1 than for Lake 12. Based on the results on the dynamics of tufa growth given by Rubinić et al. (2008), the authors hypothesized that both findings could be due to the faster temporal changes in lake morphology for Lake 1 relative to Lake 12.

b) Standing internal waves (internal seiches)

Currently, it is well known that internal seiches⁵⁵ are of much greater importance for the lake ecosystem than are surface seiches due to their much greater amplitude and effect (e.g., Bryson and Ragotzkie, 1960; Ostrovsky et al., 1996; Fricker and Nepf, 2000; Kalff, 2002). Specifically, if internal seiches become steep and unstable, or if they are disrupted by contact with underwater mounds or lake boundaries, they can induce significant currents and turbulence in the hypolimnion. Furthermore, internal seiches with large vertical amplitudes can be associated with the considerable vertical transport of water and nutrients from the hypolimnion to the epilimnion.

To date, the first and the only investigation of internal seiches in the Plitvice Lakes was performed by Gavazzi (1919). Based on temperature measurements, the author reported information about two events that occurred in Lake 12. These were seen as vertical movements of the isothermal surfaces. For the case of 23 July 1897, Gavazzi estimated the amplitude and period of about 6 m and 3.5 h, respectively, while for the second case (15 September 1915), the period was approximately two times shorter (approximately 110 min) and there was no information on the amplitude.

7. Conclusions

Generally, the underwater morphometry plays an important role in the lake dynamics, and accordingly, it affects the lake biota (e.g., Kalff, 2002). For example, as shown long ago by Gavazzi (1919), a submerged barrier in Lake 12 (Kozjak) during the summertime can produce two different vertical temperature profiles (i.e., two different stratification patterns) for the two sub-basins. Since

⁵⁵ Standing internal waves occur under the water surface due to the presence of the two layers of different densities (e.g., epilimnion and hypolimnion). Their periods can be calculated from the modified Merian's formula, where the densities of both layers are considered.

changes in the bathymetric characteristics of the Plitvice Lakes are very vivid and unsteady (Petrik, 1958; Rubinić et al., 2008), and because the ‘newest’ bathymetries of the entire lake system were determined before 1958 (Petrik, 1958), the determination of the current bathymetries of all lakes is necessary for further investigation of the dynamic processes in this lake system. The recent results of Pasarić and Slaviček (2016) also corroborate the need for the determination of the present bathymetry, especially for Lake 1 (Prošće).

There is a lack of newer investigations of the climate of the PLA. The most “recent” study (Makjanić, 1971–1972) corresponded to data that were observed in the mid-20th century. It is very likely that the climate conditions have since changed. Furthermore, an increase in the water temperature in the lakes and springs of the PLA, and in the air temperature at the site that is approximately 25 km from the PLA, was already observed for the period of 1981–2014 (Srionić et al., 2017). Furthermore, the old investigation of climate was based on time series that were too short. Therefore, the study of the current climate of the PLA is necessary. However, during the Croatian War of Independence, operational measurements within the PLA were disabled. Accordingly, meteorological, climatological and hydrological time series are incomplete. Specifically, all data for the period 1991–1995 are missing. While some data are available as of 1996, other measurements were restored even later. These heterogeneities in time series may hide true climatic patterns and, consequently, affect the quality of the conclusions of future studies. Therefore, future investigations of the climate of the PLA should be conducted with special care and should be based on the methodology of the homogenization of data series (e.g., Ribeiro et al., 2017).

The relationship between the amount of precipitation and the corresponding wind directions obtained for the PLA for the 2-year period (Babinka, 2007), as well as the distribution of stable isotopes of oxygen and hydrogen in precipitation above Croatia (Hunjak, 2015) agree well with the conclusions of Makjanić (1971–1972), which stated that the PLA is at the border between the maritime and continental climate regions.

Apart from investigations of the current state and the changes that have already been recorded in the Plitvice Lakes, the future possible impact of the anticipated warmer climate, where the quantification of the regional response of precipitation (and consequently, the hydrological cycle) to greenhouse warming is particularly challenging (Allen and Ingram, 2002, 2012), should be examined. For example, this could be done as in the study of Vrana Lake (Rubinić and Katalinić, 2014). Additionally, the establishment of a hydrodynamic model of the entire lake system coupled with hydrogeochemical model and dispersion in the lake model is highly desirable. Such a coupled model could be a helpful tool in the management and protection of this unique lake system. The present review might serve as a starting point for building such a coupled model.

In addition, for the PLA, there have been no investigations of atmospheric phenomena that are typically associated with lakes, such as lake-breeze circula-

tions. Such circulations are well investigated over larger midlatitude lakes (e.g., Harris and Kotamarthi, 2005) but can also be found over very small lakes (e.g., Asefi-Najafabady et al., 2012). Further, it is known that wintertime lake-effect precipitation events (e.g., Laird et al., 2003) can be initiated or enhanced by smaller lakes (surface area approximately 10–100 km²), although they are less intense relative to larger lakes (Laird et al., 2009, 2010). It would be interesting to inspect whether similar phenomena occur over lakes as small as the Plitvice Lakes.

Although there have been several hydrogeochemical studies of the PLA, a number of problems are still not fully understood. For example, the dynamics of the transport of dissolved matter within this complex lake system and the rates of water exchange (especially for larger lakes) are still unclear.

The hydrodynamics of the Plitvice Lakes has been poorly investigated. Therefore, further studies of physical processes within the lakes, especially of the water flow within lakes, are needed. So far, surface standing waves, which due to the small dimensions of the Plitvice Lakes have less importance for the hydrogeochemical and biological processes and conditions within the lakes, have been studied for Lake 1 and Lake 12. However, internal standing waves (internal seiches), which generally can be relevant for the vertical transport of water and nutrients from the hypolimnia to the epilimnia (e.g., Ostrovski et al., 1996), deserve further research. To date, only Gavazzi (1919) remarked on two such events observed in Lake 12 (Kozjak), while nothing is known about the same phenomenon in other lakes of the PLA. Overall, the development of a hydrodynamic model enabling the predictions of three-dimensional fields of water velocity and water temperature is highly desirable. Such a model could serve in the management and protection of the lake system.

The results of the presented investigations suggest that the Plitvice Lakes represent a dynamic, spatio-temporally variable system with respect to both the long-term and the intra-annual time scales. However, a total water volume of over 20 million cubic meters implies a certain inertness of the lake system at the intra-annual time scale.

Overall, the interconnections of complex processes and/or phenomena associated with different disciplines of earth and environmental sciences necessitate the intense collaboration of scientists from different fields. Examples of these processes and phenomena are numerous, such as the climate conditions and consequent dynamics of tufa deposition, the role of internal standing waves in the transport of nutrients within the lake, the water velocity field and the corresponding distribution of suspended matter. This further corroborates the need for the development of a hydrodynamic model for the Plitvice Lakes, and these results could serve in the investigations of problems from other earth and environmental science fields.

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APPENDIX I

Basic equations of surface seiches

For coastal waters, *i.e.*, for shallow, barotropic, homogenous fluids, the starting equations are two horizontal equations of motion, the hydrostatic equation (resulting from the vertical equation of motion for a case where there is no vertical acceleration), and the continuity equation for incompressible fluid (*e.g.*, Orlić, 2010):

$$\partial u / \partial t - fv = -(1/\rho)(\partial p / \partial x) + (1/\rho)\partial(A\partial u / \partial z) / \partial z, \quad (\text{A1})$$

$$\partial v / \partial t + fu = -(1/\rho)(\partial p / \partial y) + (1/\rho)\partial(A\partial v / \partial z) / \partial z, \quad (\text{A2})$$

$$0 = -(1/\rho)(\partial p / \partial z) - g, \quad (\text{A3})$$

$$\partial u / \partial x + \partial v / \partial y + \partial w / \partial z = 0, \quad (\text{A4})$$

where u , v and w are the x -, y - and z -components of fluid velocity, respectively, ρ is the fluid density, p the pressure, f is the Coriolis parameter, g is the acceleration due to gravity, and A is the turbulent friction coefficient. We denote an average basin depth and disturbance with D and ζ , respectively (Fig. A1). We divide (A1), (A2) and (A4) by D , and then integrate these equations over z from $z = -D$ to $z = \zeta$, while in the equation (A3), we integrate over z from $z = z$ to $z = \zeta$. Further, we assume narrow, elongated basin, for which the Coriolis force can be neglected. We also assume that the atmospheric pressure $p_a = p_\zeta$ is constant. After the substitution of $U = \frac{1}{D} \int_{-D}^{\zeta} u dz$, $V = \frac{1}{D} \int_{-D}^{\zeta} v dz$, $\tau_x = (A\partial u / \partial z)_\zeta$, $\tau_{xD} = (A\partial u / \partial z)_{-D}$, $\tau_y = (A\partial v / \partial z)_\zeta$, $\tau_{yD} = (A\partial v / \partial z)_{-D}$ and the kinematic boundary conditions at the fluid surface $w_{z=\zeta} = \partial\zeta / \partial t$ and at the basin bottom $w_{z=-D} = 0$; and finally, after neglecting nonlinear terms, we obtain the basic equations of surface seiches:

$$\partial U / \partial t = -g(\partial\zeta / \partial x) + (1/\rho D)(\tau_x - \tau_{xD}), \quad (\text{A5})$$

$$\partial V / \partial t = -g(\partial\zeta / \partial y) + (1/\rho D)(\tau_y - \tau_{yD}), \quad (\text{A6})$$

$$\partial(DU) / \partial x + \partial(DV) / \partial y + \partial\zeta / \partial t = 0. \quad (\text{A7})$$

We further assume a narrow basin of rectangular shape that is elongated in the x -direction, and has a flat bottom. After neglecting the friction and viscosity terms, we obtain:

$$\partial U / \partial t = -g(\partial\zeta / \partial x), \quad (\text{A8})$$

$$\partial(DU) / \partial x + \partial\zeta / \partial t = 0. \quad (\text{A9})$$

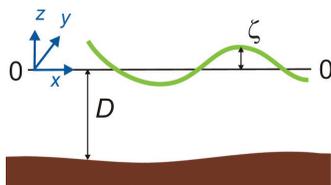


Figure A1. Sketch of an oscillation.

APPENDIX II

Analytical solution of equations of surface seiches for elongated rectangular basins and derivation of Merian’s formula

We assume wave-like solutions of the system of equations (A8)–(A9) (e.g., Orlić, 2010):

$U = \text{Re}[U_c(x)e^{-i\sigma t}]$, and $\zeta = \text{Re}[Z_c(x)e^{-i\sigma t}]$, where U_c and Z_c are amplitudes, and σ is the frequency. The substitution of U and ζ yields

$$-i\sigma U_c(x) = -g \frac{dZ_c(x)}{dx}, \tag{A10}$$

$$D \frac{dU_c(x)}{dx} - i\sigma Z_c(x) = 0. \tag{A11}$$

Equation (A11) gives $Z_c(x) = \frac{D}{i\sigma} \frac{dU_c(x)}{dx}$. We substitute $Z_c(x)$ into equation (A10). Thus, we obtain a wave equation

$$\frac{d^2U_c(x)}{dx^2} + \kappa^2 U_c(x) = 0, \tag{A12}$$

where $\kappa^2 = \frac{\sigma^2}{gD}$. Generally, a solution of the equation is of the form $U_c(x) \sim e^{\alpha x}$. Accordingly, the characteristic equation of (A12) is $\alpha^2 + \kappa^2 = 0$ and consequently, $\alpha = \pm i\kappa$. Thus, the solution of (A12) is

$$U_c(x) = Ae^{i\kappa x} + Be^{-i\kappa x}, \tag{A13}$$

where amplitudes A and B are complex numbers ($A, B \in \mathbb{C}$). Boundary conditions for surface seiches in the closed basin impose no horizontal speed at basin bound-

aries $U_c(x=0, L) = 0$, where L is the basin length. For $x=0$ this yields $A = -B$, and accordingly, $U_c(x) = A(e^{ikx} - e^{-ikx}) = 2A\sin(\kappa x)$ while for $x=L$ we obtain $e^{i\kappa L} - e^{-i\kappa L} = 0$ and thus $\sin(\kappa L) = 0$, that is $\kappa = \kappa_n = \frac{n\pi}{L}$, where n is a natural number ($n \in \mathbb{N}$) that denotes an ordinal number of the wave mode. Thus $U_c(x) = 2A\sin(\kappa x) = a_n e^{ib_n} \sin(\kappa_n x) = U_{cn}(x)$, where $2A_n = a_n e^{ib_n}$ and A_n is a discrete value of A that corresponds to the n^{th} mode.

We substitute $U_{cn}(x) = a_n e^{ib_n} \sin(\kappa_n x)$ into the initially assumed solution $U = \text{Re}[U_c(x)e^{-i\sigma t}]$. This yields $U = U_n = \text{Re}[U_{cn}(x)e^{-i\sigma_n t}] = \text{Re}[a_n e^{ib_n} \sin(\kappa_n x)e^{-i\sigma_n t}] = \text{Re}[a_n \sin(\kappa_n x)e^{-i(\sigma_n t - b_n)}]$. Similarly, for the discrete values of the amplitude $Z_c(x) = \frac{D}{i\sigma} \frac{dU_c(x)}{dx}$ we obtain $Z_{c,n}(x) = \frac{D}{\sigma_n} a_n e^{ib_n} \kappa_n \cos(\kappa_n x)$. The substitution of $Z_{c,n}(x)$ into $\zeta = \text{Re}[Z_c(x)e^{-i\sigma t}]$ yields $\zeta_n = \text{Re}\left[\frac{D}{\sigma_n} a_n e^{-i(\sigma_n t - b_n)} \kappa_n \cos(\kappa_n x)\right]$. Finally, for the narrow rectangular closed basin we obtain

$$U_n = a_n \sin(\kappa_n x) \sin(\sigma_n t - b_n), \quad (\text{A14})$$

$$\zeta_n = a_n \frac{D}{\sqrt{gD}} \cos(\kappa_n x) \cos(\sigma_n t - b_n), \quad (\text{A15})$$

where $\kappa_n = \frac{n\pi}{L} = \sqrt{\frac{\sigma_n^2}{gD}} = \frac{\sigma_n}{\sqrt{gD}}$ is the wave number and $\sigma_n = \kappa_n \sqrt{gD} = \frac{n\pi}{L} \sqrt{gD}$ is the angular frequency of the n^{th} normal mode, while an amplitude of oscillation a_n and a phase b_n are the constants that depend on the initial conditions. Finally, from the angular frequency we obtain a period of the n^{th} mode

$$T_n = \frac{2\pi}{\sigma_n} = \frac{2\pi}{\frac{n\pi}{L} \sqrt{gD}} \text{ which yields}$$

$$T_n = \frac{2L}{n\sqrt{gD}}. \quad (\text{A16})$$

The period of the first harmonic $T = \frac{2L}{\sqrt{gD}}$ was first derived by Merian in 1828 (e.g., Stewart, 1964). Merian's formula is strictly valid for an idealized, rectangular basin. Still, it can be used to estimate the period of dominant seiches in lakes of irregular depth if the geometry of the basin is relatively simple (Rueda and Schladow, 2002). In that case, the mean depth is employed.

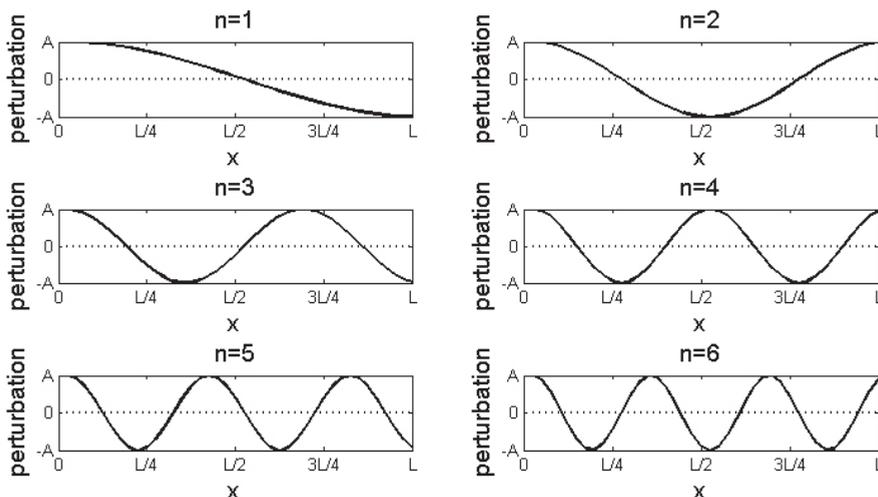


Figure A2. Illustration of the first six normal modes ($n = 1, 2, \dots, 6$) for a narrow rectangular basin at initial moment $t = 0$ (Eq. A15). Basin length and depth are L and D , respectively, while $a_n = 1$ and $b_n = 0$ are assumed for all six modes. Dotted lines indicate mean water levels, while maximum water surface displacement is A .

SAŽETAK

Pregled istraživanja Plitvičkih jezera u područjima meteorologije, klimatologije, hidrologije, hidrogeokemije i fizičke limnologije

Zvezdana Bencetić Klaić, Josip Rubinić i Sanja Kapelj

U jezerima se istovremeno događa više međusobno povezanih fizičkih, kemijskih i bioloških procesa. Stoga istraživanje jezera zahtijeva multidisciplinarni pristup koji uključuje fiziku (uključujući i fiziku atmosfere–meteorologiju), kemiju, geologiju, hidrogeologiju, hidrologiju i biologiju. Svaka od tih disciplina proučava jezero sa svog stanovišta. Ipak, studije jezera, koje primarno pripadaju jednoj disciplini, zbog neizbježne veze proučavanog fenomena s drugim disciplinama, bar donekle izvještavaju o rezultatima

važnim za druge discipline. Plitvička jezera su jedinstven kaskadni lanac krških jezera te su do sada bile predmet istraživanja brojnim autorima. Ovdje dajemo pregled studija koje obuhvaćaju meteorološka, klimatološka, hidrološka i hidrogeokemijska istraživanja te istraživanja u okviru fizičke limnologije, a odnose se na područje Plitvičkih jezera (PLA). Cilj nam je objediniti rezultate svih tih disciplina i učiniti ih dostupnima znanstvenicima drugih srodnih disciplina, kako bi olakšali daljnja istraživanja PLA u području prirodnih znanosti. Dodatno, vrijedni rezultati ranih istraživanja Plitvičkih jezera općenito su nedostupni široj znanstvenoj zajednici te su pisani hrvatskim jezikom. Stoga ovdje dajemo njihov sažetak te ih stavljamo na raspolaganje širem krugu čitatelja.

Ključne riječi: sliv, geoznanosti, hidrodinamika, krš, sedrene barijere

Corresponding author's address: Zvezdana B. Klaić, Department of Geophysics, Faculty of Science, University of Zagreb, Horvatovac 95, 10000 Zagreb; e-mail: zklaic@gfz.hr



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