

Research Article

Groundwater Quality on the Adriatic Karst Island of Mljet (Croatia) and Its Implications on Water Supply

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Received 18 July 2018; Revised 29 October 2018; Accepted 25 November 2018; Published 4 March 2019

Guest Editor: Ariadne Argyraki

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Water supply of the islands is a global challenge, especially in the countries which have highly indented coastlines with numerous islands. The island of Mljet in Croatia was investigated due to its unique source of water supply: desalination of water from brackish lakes—*blatinas*—fed by groundwater and connected to the sea by karst conduits. Water sampling and chemical analyses were performed during hydrological minimum and maximum with regard to groundwater levels in 2005/2006 and minimum in 2016. A total of 13 samples were analysed within the study: 10 samples were taken from *blatinas*, 1 from pit well, and 2 from borehole wells. All waters sampled from the lakes are of Na-Cl type. The seawater percentage in the lakes used to extract feed water for desalination plants, calculated by conservative mixing approach, is relatively low (0.7–9.8%) and varies in correlation with hydrological seasons. Low proportion of seawater is an essential factor of cost minimisation in desalination by the installed reverse osmosis (RO) plants. Daily monitoring of total dissolved solids in the feed water was introduced in May 2016, and its results were analysed in the context of precipitation—a sole source of island aquifer recharge. Maximum concentrations were observed during September and interpreted to be caused by a combination of natural and anthropogenic pressure during the summer tourist season. Minimum concentrations were expected after the rainy season in the cold part of the year but were observed in June instead. Due to a short observation period and untypical distribution of precipitation in the same time interval, the data can only be considered indicative. An unusual pattern of sulphate anion concentrations, which cannot be attributed solely to fresh- and seawater mixing, was observed in one of the *blatinas*, but its origin could not be determined based on available data. Taking into account all the presented data on groundwater quality, climate change predictions, the connection of water supply system to the mainland and problems with the effluent treatment, it is clear that the main future challenge will be the creation of an island-wide sustainable water management plan followed by continuous monitoring and research.

1. Introduction

Islands make up about 1/6 of the land area on Earth [1]. The majority of that area is composed of large islands such as Greenland, New Guinea, Borneo, Madagascar, Sumatra, or Honshu. They also house a significant proportion of the world population, ca. 700 million or 10% [2], with the most populous being Java, Honshu, Great Britain, Luzon, and Sumatra. However, there are many small (<1000 km²) and very small islands (<100 km² or width ≤ 3 km) [3], many of which are distant from the mainland. According to [4], forty islands in the Mediterranean region can be classified as small, and far more as very small islands, according to mentioned UNESCO classification [3]. Unlike large islands, they often

lack single or multiple resources and are therefore faced with a specific set of challenges. It is their strategic interest to reach self-sufficiency in different aspects, especially regarding water and energy supply. Such strategies often combine both aspects in the systems including desalination and utilization of renewable energy sources. Twenty islands worldwide are trying to achieve an absolute water and energy self-sufficiency, out of which ten have already succeeded [2, 5].

Desalination is a source of water supply in many regions worldwide, with the predominance of arid and coastal areas, as well as small and/or remote islands. There are approximately 24,000 desalination plants in more than 150 countries, and the number is continuously growing by about

500 plants annually. Over half of them are situated in the Middle East, followed by 17% in North America and 10% in Europe. Two-thirds of all installed desalination plants use RO technology [6].

Croatia has one of the most indented coastlines on a global scale (indentation index being 3.4 [7]), comprising 79 islands, 525 islets, and 642 rocks and rocks awash, which makes a total of 1,246 [8]. It can be characterized as concordant coastline, i.e., the beds of different rock types are folded into ridges, which are oriented parallel to the coastline. Concordant coastlines can be present as two different types, one of which is designated the Dalmatian type coast [9], after the Croatian region of Dalmatia, where the island of Mljet is also situated (Figure 1). A typical feature is that the islands, straits, and peninsulas are elongated parallel to the shoreline, and elongated shape obviously has implications to the possibility of fresh water accumulation in the island aquifers.

At the beginning of the 2000s, a bulk research program was performed on several small (even for the Adriatic Sea scale) islands in the northern part of Dalmatia. The program comprised geological and hydrogeological mapping, surface geophysical research (mostly electric resistivity tomography and seismic refraction profiling), and borehole drilling with pumping tests and hydrochemical research. The main purpose was to extract brackish groundwater with the lowest possible proportion of seawater in order to minimise the cost of desalination by RO plants. Results were limited to a few positive boreholes, but the experience gained was significant for further studies, e.g., [10–12], and numerous unpublished technical reports. Unfortunately, the program was stopped and has not been renewed since.

Among 66 permanently inhabited Croatian islands [8], ten have secured their water supply from their own resources (partially or completely). Several studies have been performed on these and some other islands [13, 14]. RO desalination plants exist on the islands of Dugi otok, Lastovo, and Mljet (Figure 1). While all of these islands use brackish water from drilled wells, the latter gets the majority of feed water from specific natural brackish lakes—*blatinas*. Being that the *blatinas* are the main water source used for public water supply, the quality of their water and groundwater in connected aquifers is paramount for the island's self-sufficiency. Taking that into account, the main goal of the presented study is to establish a scientific basis for understanding these unique natural phenomena and their connection with the groundwater in the surrounding karst aquifers. The obtained results can be used to improve water supply of the island of Mljet, despite other possible solutions, since the complete (or partial) water supply from its own resource is a very important present and future task.

2. History of Hydrogeological Studies on the Island of Mljet

The island of Mljet has a surface of 98 km². It is elongated in WNW-ESE direction and has an indentation index of 3.81 [10], which is calculated as the ratio between the actual coastline length and the circumference of the circle with the area equal to the island surface area [7]. It is a part of southern

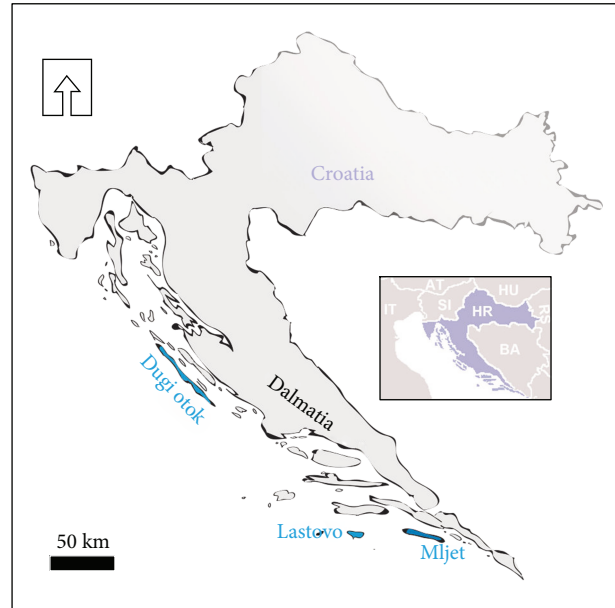


FIGURE 1: Position of Croatia on the Adriatic coast of SE Europe and the island of Mljet in S Dalmatia region (AT: Austria; BA: Bosnia and Herzegovina; HR: Croatia; HU: Hungary; IT: Italy; RS: Serbia; SI: Slovenia).

Dalmatian island archipelago and is characterized by a semi-arid variety of Mediterranean climate, i.e., Csa according to Köppen classification [15].

The earliest data about the hydrogeological research of the island of Mljet come from [16] and were conducted in order to ensure local water supply. At that time, the population of the island was small, and rainwater harvesting tanks were mostly used. The authors described low-discharge freshwater springs and proposed geophysical research which would determine the locations for two exploration-exploitation wells targeting dolomites in the vicinity of Babino Polje. At the same time, the *blatinas* were deemed unfit for water supply purposes and no further research was recommended. However, construction of a dug well next to *blatina* in Blatsko polje was proposed; the location of which would be determined by detailed hydrogeological mapping and geophysical research.

In 1971, four exploration wells were drilled on the island [17]. The investor, the local government, chose the locations and drilled the wells without prior hydrogeological research and supervision. Unsurprisingly, the wells did not show any significant yield (maximum was 0.2 l/s).

Hydrogeological research and pumping tests at a few localities were conducted by [18] in order to secure water for the temporary water supply using RO desalination plants, as a transitional solution until the regional Neretva-Pelješac-Korčula-Lastovo (NPKL) pipeline is extended from the mainland to Mljet island. The research has shown favourable conditions, and RO desalination plants were installed in Sobra, Blato, and Kozarica (Figures 2 and 3). After that, an additional well in Blato was drilled and tested in 2000 [21]. It had very good characteristics so the temporary water supply was improved. Similar procedure increased

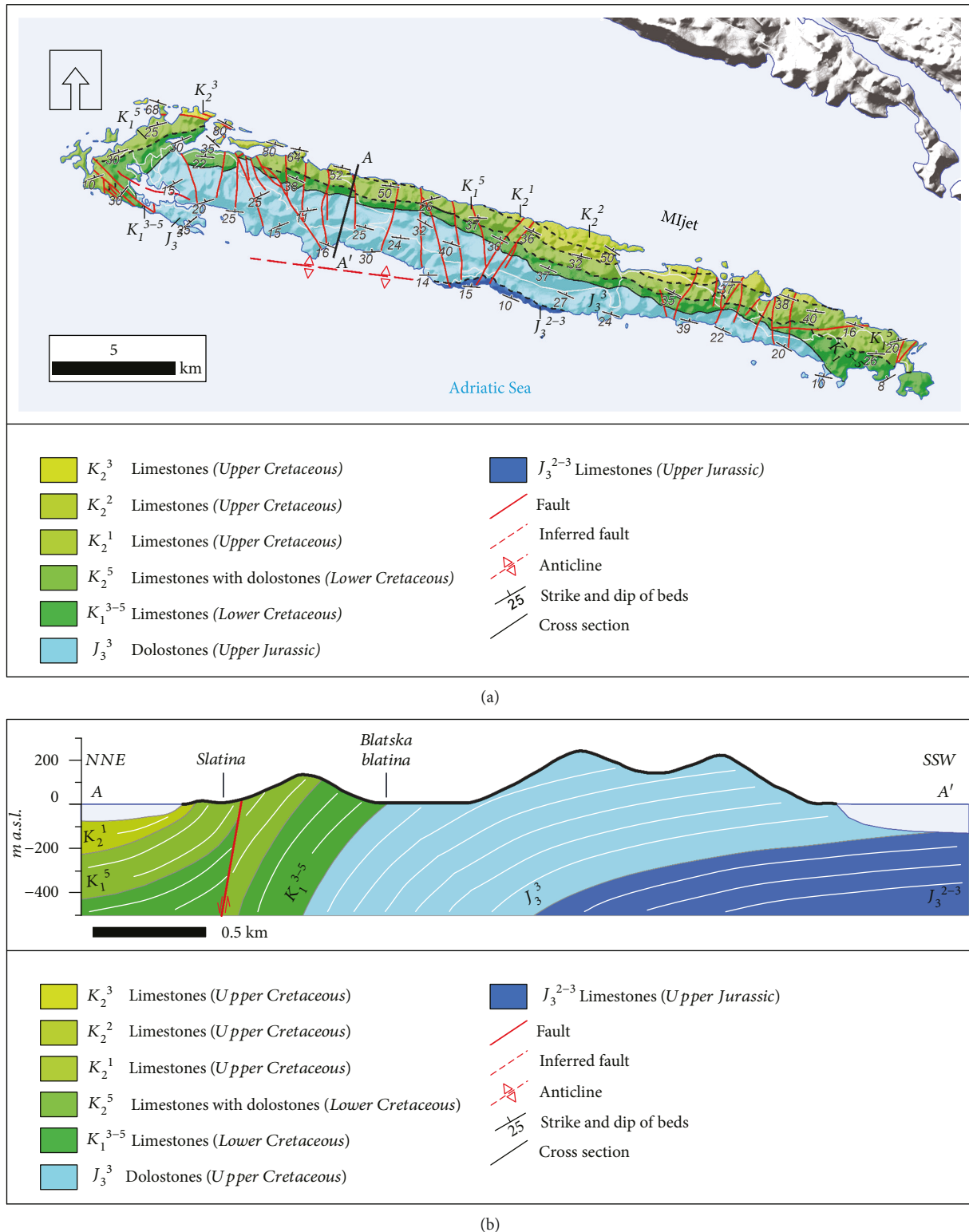


FIGURE 2: Geological map (a) and cross section (b) of the island of Mljet (modified after [19, 20]).

the intake capacity in Sobra in 2002 [22]. Sobra desalination plant is situated close to the coast so it discharges its effluent into the sea, while the one in Blato is in the central part of the island so the effluent is disposed of in the same karst polje.

Although a branch of NPKL pipeline to the island of Mljet (NPKLM) was partially constructed several years ago, it was put into operation only recently and the water supply for the settlements is still secured using desalination of brackish water from lakes and wells. The supply exceeds demand

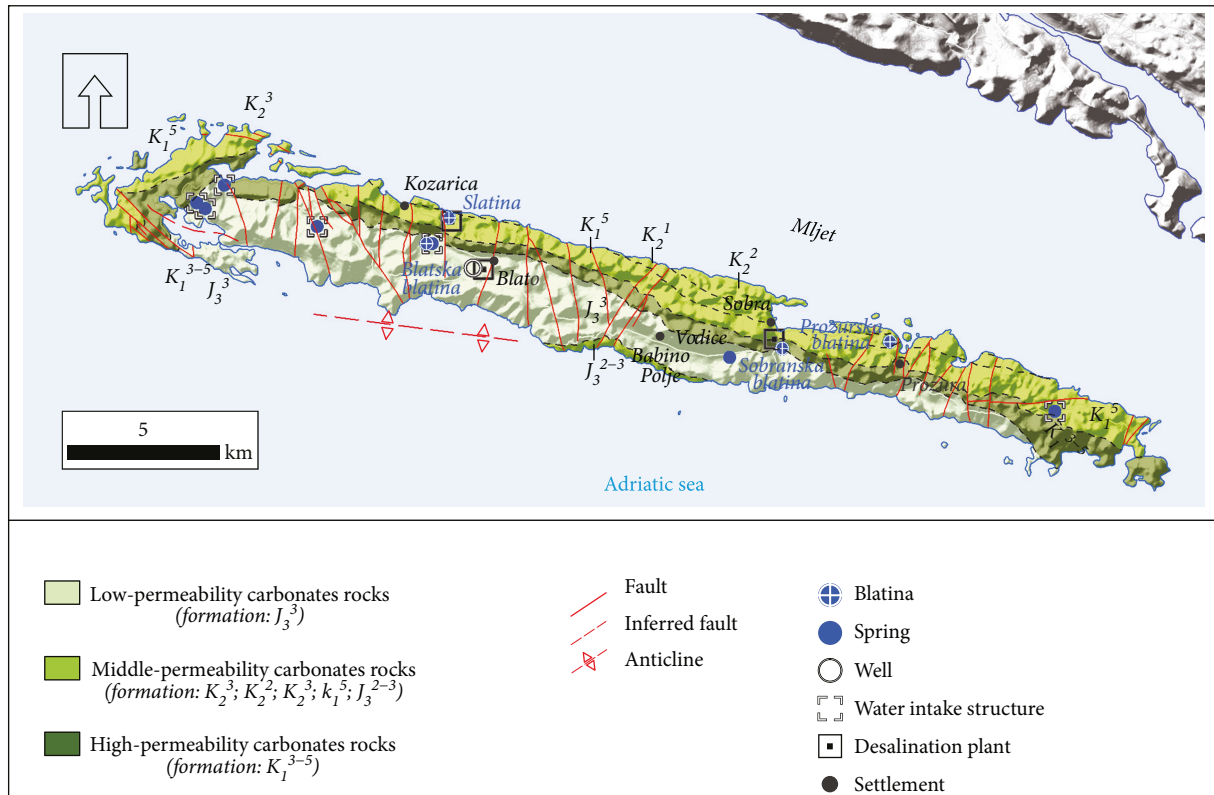


FIGURE 3: Hydrogeological map of the island of Mljet (modified after [19, 20]).

by far during the cold part of the year. In the warm period of the year, the island population multiplies due to tourism activity, which is characteristic of many Mediterranean islands [23]. At the same time, the groundwater level is at its minimum, so the desalination plants usually cover 90% of the demand, while the rest of the demand is met using water carrier ships.

3. Geological and Hydrogeological Settings

3.1. Structural Setting and Lithostratigraphy. Structural fabric of Mljet is basically simple: it is a monocline dipping toward NNE, probably a northern limb of an overturned anticline (Figure 2). Its strike is WNW-ESE, and the axis is supposed to be off the SW shore of the island, i.e., the whole overturned southern limb is submerged under the sea [19]. The only prominent fault is a reverse fault along the SW shore of the island, which is also submerged. It is a marginal fault which penetrated deep in the lower structural units of the Dinarides inside the Adriatic (Vis-Lastovo-Mljet fault), while the fault contact with the Adria microplate is about 10 km off the SW coast of Mljet (Vis-southern Adriatic fault; [10, 24]). The majority of faults have normal and high angle strike relative to the fold axis. Although numerous, they are not very persistent, so the dominant fold structure is mostly preserved.

Chronostratigraphic units are presented according to [19]. The oldest deposits on Mljet are of Jurassic age, and they crop out on the SSW limb of the island (Figure 2). Kimmeridgian-Tithonian deposits (J_3^{2-3}) are fine-grained limestones, deposited mechanically (calcilutite), with high

CaCO_3 content, and their thickness is around 250 m. However, the most characteristic Jurassic deposits are Tithonian dolostones with rare occurrences of interlayered limestone (J_3^3). Dolomitization process destroyed the majority of primary limestone structures, but in some localities, calcilutites were identified. The thickness of the deposits is around 800 m.

Lower Cretaceous deposits also extend in a WNW-ESE belt along the northern shore of the island (Figure 2). Barremian and Aptian deposits (K_1^{3-5}) lay transgressively on the Malmian deposits. They are mechanically deposited calcilutites and calcarenites. Calcilutites are composed of up to 98% CaCO_3 , and biocalcarenites contain well-sorted material. Thickness is up to 400 m. Albian limestones (K_1^5) have different fossil content, contain dolomite interlayers, and are around 200 m thick.

Upper Cretaceous deposits extend all along the northern coast of the island (Figure 2). They are lithologically very similar to Lower Cretaceous deposits but can be distinguished by micro- and macrofossil content. Cenomanian and Turonian deposits (K_2^1 and K_2^2 , respectively) are present on Mljet itself, while Senonian (K_2^3) are submerged, but can be found on the islets off the northernmost coast of Mljet.

Tertiary deposits are not present on Mljet, and the Quaternary is represented by *terra rossa* and eolian sands in small karst poljes.

3.2. Hydrogeological Setting. The abovementioned Jurassic and Cretaceous limestones and dolostones can be characterized by different hydrogeological properties and functions

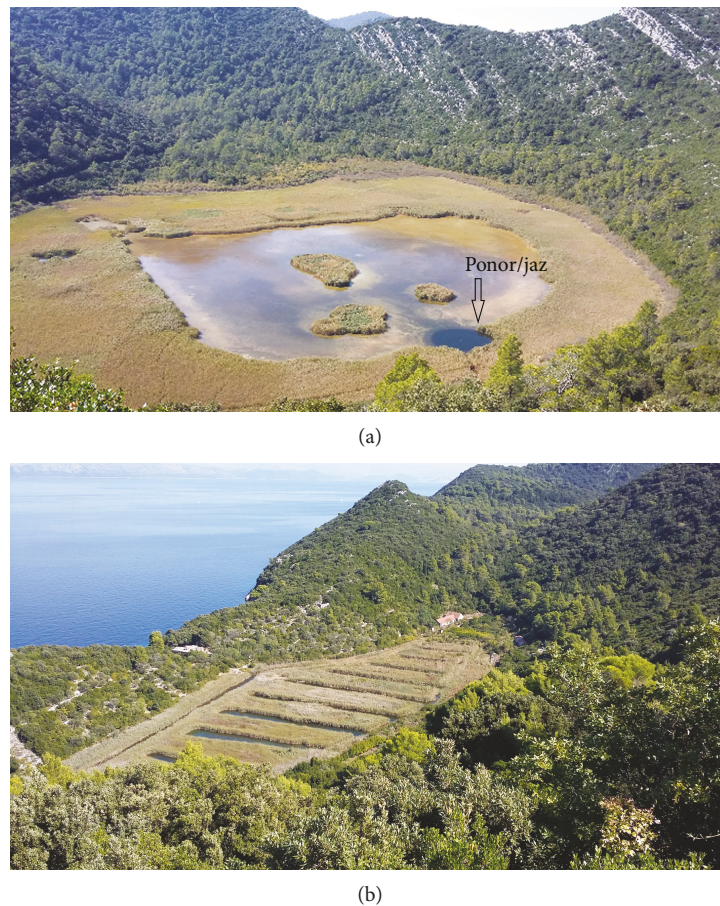
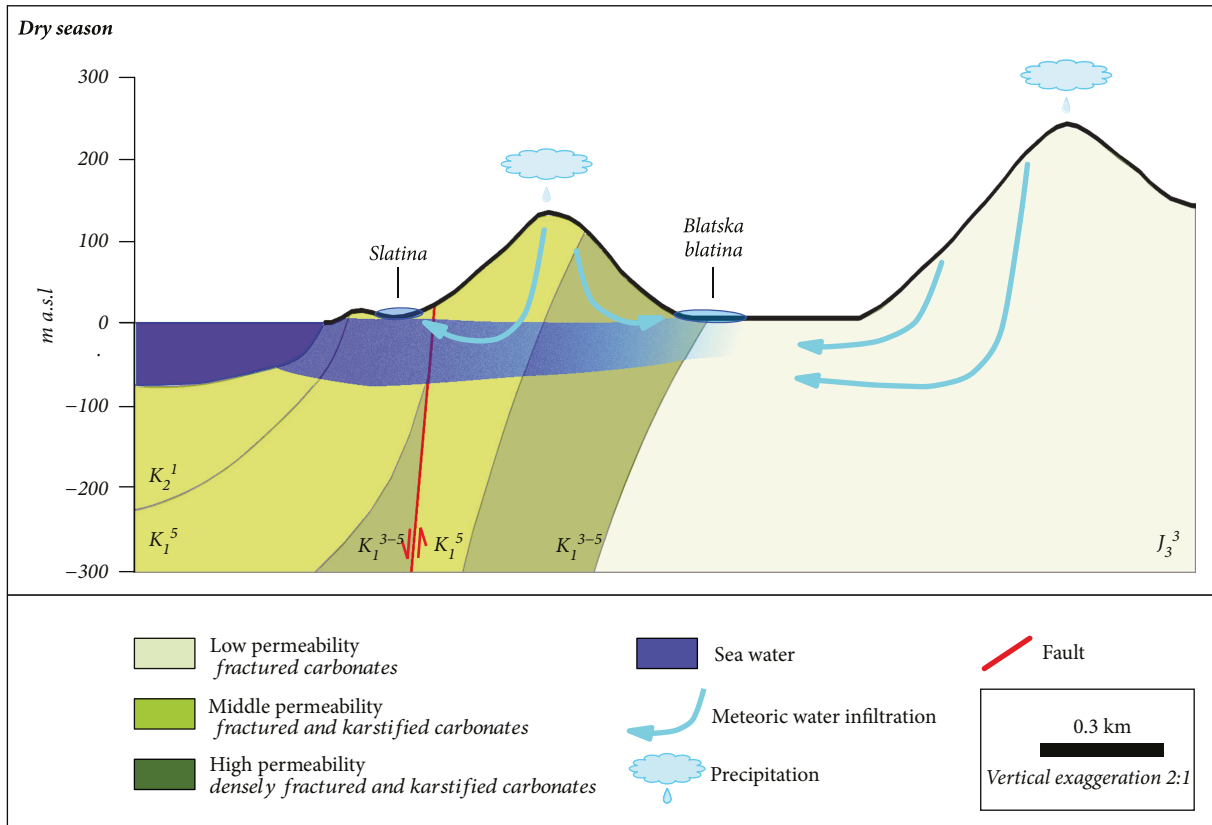


FIGURE 4: Blatska blatina in Blato—situated furthest from the sea (a) and blatina Slatina in Kozarica—closest to the sea both laterally and vertically and with known conduit toward the sea (b).

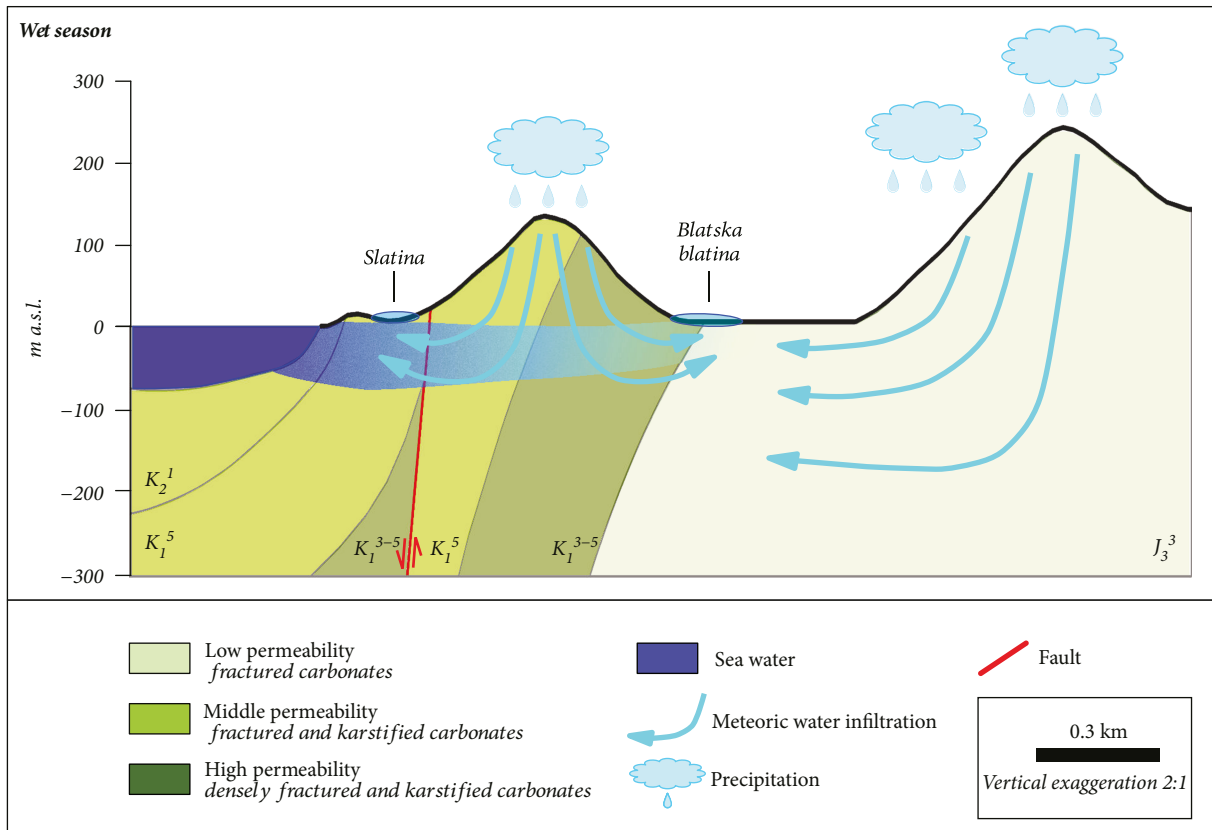
(Figure 3). The dominant type of porosity is secondary porosity induced by fracturing. In limestones, the fracturing was followed by intense karstification, which is far less pronounced in the dolostones. It is important to point out that in the Dinaric karst, the karstification is much deeper than it would be expected when observing present-day sea level. The mean sea level was over 100 meters lower than today at the end of the last glacial maximum, thus making the base of karstification lower as well [25–28]. Such sequence of events obviously caused the existence of karst channels below present-day sea level, which has a significant impact on flow in karst aquifers [29]. On the surface, the limestone is more prone to corrosion which results in typical karst forms, while the dolomite is predominantly mechanically weathered into milder morphological forms. On the islands of such size, relatively lower permeability of the rock mass (dolomitic limestones or dolostones) is more suitable for fresh or brackish water accumulation in the underground than the highly karstified limestones. That is the case because in the highly permeable rock mass, total seawater intrusion would occur and there would be no aquifers or lenses of fresh groundwater significant in the context of providing public water supply.

Because of the permeability contrast between Jurassic (predominantly) dolostones and Cretaceous (predominantly) limestones, the dolostones represent a relative hydrogeological

barrier on the island [30, 31]. Monocline structure dipping toward NNE, combined with the island's elongated shape and zonal arrangement of geological units with dolostones in the SW and limestones in the NE, causes the water which infiltrates into carbonate rock mass to flow toward the NE and discharge along the NE coast in the concentrated form of *vuljas* (submarine springs) and coastal springs of increased salinity [18], as well as via diffuse discharge, i.e., seepage [10]. Although dolomitic rocks are declared a relative barrier, their persistent fracturing produces a bulk hydraulic conductivity that is one order of magnitude lower than the karstified limestones. This combination of factors makes them adequate for (1) preventing significant seawater penetration into island aquifer from the S and (2) generating slower flux through dolostone rock mass, thereby creating certain groundwater storage which slowly discharges toward the northern parts in dry seasons due to aforementioned structural, geological, and morphological reasons. In such conditions, the *blatins* and karst aquifers can exist in both dolomites and limestones. If the island consisted exclusively of karstified limestone rock masses of high hydraulic conductivity, there would be no possibility to prevent an almost immediate discharge of the infiltrated water (and groundwater) during rain periods due to the short distance between the infiltration area and the sea. Furthermore, seawater would extensively intrude



(a)



(b)

FIGURE 5: Conceptual models of blatinas during dry (a) and wet (b) periods.

the rock masses during dry periods inhibiting its prolonged mixing with freshwater.

Although there are some minor permanent and intermittent freshwater springs on the island, the most impressive phenomenon from the hydrogeological point of view is the *blatinas* (Figure 4). These are marshy brackish lakes situated next to ponor (swallow hole) of karst polje (as in Blatsko polje) or submerged sinkholes (as in Sobra, Kozarica, and Prožura).

Each *blatina* has ponor, locally named *jaz*—a deep shaft that continues through the unexplored karst conduits and has contact with the sea, which is evident from the regular appearance of eels in *blatinas*. *Jaz* functions as an estavelle connected to the sea. During low groundwater levels, the seawater/freshwater transition zone progresses deeper inland and penetrates the aquifer, causing an increase in groundwater salinity which also reaches *blatinas*. During high groundwater levels, fresh water sinks into *jaz* and pushes the mixing zone toward the sea, causing a decrease in *blatina* salinity. Functioning of *blatinas* during different hydrological seasons is schematised in Figure 5.

Even though in the Adriatic there are islands of similar size, shape and hydrological parameters (as summarized by [4, 10] into a hydrological size index), *blatinas* appear exclusively on Mljet. It is a consequence of a characteristic combination of hydrogeological and morphological features, i.e., of the facts that (1) the altitudes of polje and sinkholes are very close to sea level and (2) polje and sinkholes are connected to the sea by macroscopic size karst conduits.

4. Methodology

Water samples were collected during two separate campaigns. A set of samples was collected during hydrological minimum (autumn of 2005) and hydrological maximum (spring 2006), with regard to groundwater levels, at different kinds of hydrogeological features: *blatinas*, pit well, and drilled wells. These samples were analysed in the hydrochemical laboratory of the Croatian Geological Survey. The electrical conductivity (EC), total dissolved solids (TDS), pH, and temperature (T), as well as the alkalinity of all the samples, were measured *in situ*. Contents of sulphate, nitrate, bromide, potassium, sodium, calcium, and magnesium were analysed using LabAlliance ion chromatography apparatus. Chloride content was determined by the addition of dilute mercuric nitrate solution to acidified water in the presence of diphenylcarbazone indicator. Data quality was assessed by calculating the charge balance between the sum of cations and the sum of anions, expressed in meq/l, which was always $\pm 5\%$.

Another sampling was conducted in 2016 from Sobranska *blatina*. This sample was analysed by NALCO Water laboratory in Leiden, The Netherlands, certified to ISO 9001 standard.

TDS of feed water from Sobranska *blatina* was monitored on a daily basis by the operator of the desalination plant in Sobra from May 2016 to June 2018 and

monthly average TDS values were calculated as the arithmetic mean.

The data from sampling campaigns in 2005/2006 were subjected to mathematical multivariate technique (R-mode factor analysis) together with samples from numerous Adriatic islands [12]. The result was a “minimum” mathematical model which ignores minor influences and nonlinear effects present in the data spread [32]. Through this technique, the multivariate relationships were reduced to simple correlations with a number of mutually uncorrelated and independent factors. In that way, data structure hidden from direct observation can be recognized and explained as natural processes in the system. Such analysis is often used in hydrogeological and environmental studies for estimating the source of pollution and for various similar purposes [33–37]. For this purpose, software STATISTICA 7.0 was used.

All precipitation data were obtained from the Meteorological and Hydrological Service of Croatia which has a climatological station on the island of Mljet. Precipitation was also recorded on a daily basis and afterwards summed into monthly precipitation.

5. Results and Discussion

5.1. Hydrochemical Facies. Hydrochemical analyses from water sampling during hydrological minimum 2005, maximum 2006, and minimum 2016 are displayed in Table 1 and Figure 6.

It is visible that the nontreated waters during the hydrological minimum do not satisfy the prescribed criteria for drinking water. All of the samples exceed maximal allowed concentrations of sodium and chloride ions, as well as EC, which is in accordance with all known facts about the genesis and functioning of *blatinas*. Also, in Blato wells and Prožurska *blatina*, the sulphate ion concentrations exceed maximum values.

High nitrate ion concentrations were also observed in *blatinas*, especially during higher groundwater levels. That is attributed to the leaching of the nitrates from soil on arable land in karst poljes and from the epikarst zone during a rainy period of the year. Also, in such marshy lakes, a significant amount of nitrogen is present in living plants and animals, as well as in their detritus. Ammonification and nitrification occur during their decomposition, which additionally increases the nitrate content in the waters.

The Piper diagram (Figure 6) illustrates the hydrochemical facies of analysed waters. It is visible that 11 out of a total of 13 analysed samples exhibit a sodium-chloride facies. Water from Vodice spring is (Ca, Mg)-HCO₃ type during both dry and wet seasons and its composition reflects the Jurassic dolomite aquifer from which the water originates (Figures 2 and 3). Water from wells in Blato is the only one which changes the type seasonally: during the hydrological maximum, it exhibits a mixed-HCO₃ type facies, although clearly much higher concentrations of calcium and magnesium cations are present than in other analysed waters.

TABLE 1: Physicochemical parameters and major ion composition of waters from localities on the island of Mljet in different seasons (values in **bold italics** are exceeding maximum values for drinking water; localities marked by an asterisk are not a part of the water supply system).

	Sampling point	Elevation (m a.s.l.)	EC ($\mu\text{S}/\text{cm}$)	T ($^{\circ}\text{C}$)	pH	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	HCO ₃ ⁻ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	NO ₃ ⁻ (mg/l)
MIN 2005	Spilja intake structure—Sobra	4	2,860	15.7	7.4	153	53.2	329	9.8	399	660	90	1.9
	Blato wells	28	8,120	15.9	7.66	160	117	1,574	76	410	2,240	300	0
	Slatina	0.5	6,930	22.1	7.5	118	111	1,096	70	450	1,950	190	0
	Prožurska blatina*	0.5	32,000	26.1	7.79	75	200	5,582	102	310	9,640	1,600	0
MAX 2006	Spilja intake structure—Sobra	4	1,527	15.7	7.61	66.4	20.9	185	3.1	215	340	50	0
	Sobranska blatina	3	1,529	16.2	7.82	66.4	20.9	195	3.1	215	380	51	0
	Blato wells	28	877	14.7	7.59	76.8	25.4	46	2.1	285	86	43	29
	Blatska blatina	2	2,010	14.6	8.23	78.4	25.1	380	3.2	285	754	46.9	39
	Kozařica intake structure	1	5,620	15.2	7.24	126.4	90.8	728	3.4	510	1,436	50.1	32
	Slatina	0.5	6,550	14.7	7.26	127.6	90.6	891	3.4	510	1,781	42.5	22
	Prožurska blatina*	0.5	17,170	19.6	8.5	171.2	338.9	2,520	52	580	4,889	430	0
	Vodice spring*	103	762	14.4	7.55	80.8	35.2	24	1.2	290	47.6	11.2	0
	Spilja intake structure—Sobra	4	3,300	—	8.2	140	61	410	15	280	790	100	<10
	Drinking water		2,500	25	6.6-9.5	n/a	n/a	200	12	n/a	250	250	250

Sources: data for 2005 and 2006 [10]; standards for drinking water [38]. Abbreviations: MIN: hydrological minimum; MAX: hydrological maximum; both with respect to groundwater levels.

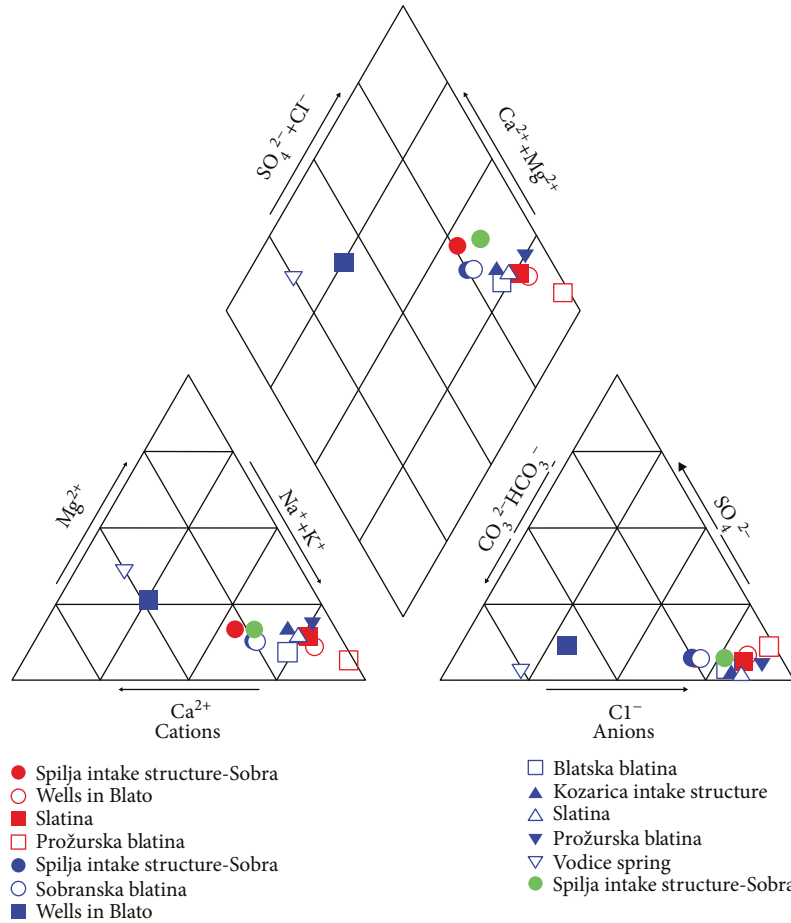


FIGURE 6: Piper diagram constructed from major ion compositions of samples shown in Table 1 (red symbols: MIN 2005; blue symbols: MAX 2006; green symbol: MIN 2016).

During the drilling, Musladin [21] reported that the well is in limestone rock up to its final depth of 38 m, but the water composition suggests that contact with dolomite exists, and probably in close proximity, as suggested by geological setting (Figure 2(b)).

5.2. *Seawater Percentage.* The percentage of seawater (SP) was calculated according to conservative mixing approach [39], from measured concentrations of Cl^- ions, using the simplified form of the equation according to [12]:

$$SP = 0.005[Cl^-]. \tag{1}$$

Equation (1) is a theoretical linear equation describing the relation of seawater percentage in the sample to chloride anion content in the sample valid for coastal mixing (transition) zone. The equation is simplified by the following assumptions: (i) concentration of chloride anions in rainwater is zero; (ii) concentration of chloride anions in the seawater is constant; and (iii) the only source of chlorides in groundwater is mixing with seawater. Notwithstanding these simplifications, the equation is adequate for orientation purposes, especially in the context of other necessary simplifications while considering karstified carbonate aquifers and island aquifers.

TABLE 2: SP in the samples from different locations and in different seasons on the island of Mljet.

	Location	SP (%)
MIN 2005	Spilja intake structure—Sobra	3.3
	Wells in Blato	11.2
	Slatina	9.8
	Prožurska blatina	48.2
MAX 2006	Spilja intake structure—Sobra	0.7
	Sobranska blatina	1.9
	Wells in Blato	0.4
	Blatska blatina	3.8
	Kozarica intake structure	7.2
	Slatina	8.9
MIN 2016	Prožurska blatina	24.4
	Vodice	0.2
MIN 2016	Spilja intake structure—Sobra	4.0

Source: data for 2005 and 2006 from [10]. Abbreviations as in Table 1.

As can be observed in Table 2, the lowest percentage was recorded in the natural spring of Vodice (0.2%), and the wells in Blato (0.4%), which was expected. Blatinas generally have

TABLE 3: Factor scores. Specific objects are described by three dominant factors/processes.

MIN 2005				MAX 2006			
Location	F1	F2	F3	Location	F1	F2	F3
Spilja intake structure—Sobra	-0.125	0.725	0.497	Spilja intake structure—Sobra	-0.329	-1.023	0.478
Wells in Blato	1.267	0.786	0.768	Sobranska blatina	-0.362	-1.034	0.767
Slatina	0.810	1.044	1.740	Wells in Blato	-0.201	-0.654	-0.578
Prožurska blatina	5.140	-0.637	1.059	Blatska blatina	0.038	-0.842	-0.418
<i>Dominant process in the system (in italics)</i>				Kozarica intake structure	0.583	0.857	-0.878
				Slatina	0.680	0.780	-0.689
<i>Very dominant process in the system (in bold italics)</i>				Prožurska blatina	2.295	1.903	2.328
				Vodice spring	-0.434	-0.580	0.320

Source: [10]. Abbreviations as in Table 1.

TABLE 4: Measured and theoretical sulphate anion concentrations in mg/l.

	Measured	Calculated from SP	Calculated from [Cl ⁻]
Wells in Blato (MIN 2005)	300	302	307
Prožurska blatina (MIN 2005)	1,600	1,301	1,269
Prožurska blatina (MAX 2006)	430	659	652

Abbreviations as in Table 1.

higher SP, which is logical due to their proven conduit connections to the sea: Sobranska blatina (1.9%), Blatska blatina (3.8%), and Slatina (9%). The highest SP was recorded in Prožurska blatina (24.4–48.2%, depending on the season), which is not included in the water supply system. That would not be economically feasible due to the fact that the energy consumption for RO desalination, and consequently the cost, increases exponentially with water salinity.

5.3. Multivariate Factor Analysis. The hydrochemical data from 79 samples from various Croatian Adriatic islands were subjected to multivariate analysis technique of factor analysis [12], which has shown that 13 hydrochemical variables can be grouped into three factors, which represent 84% of the total variance of the system when considering Adriatic karst islands in general. Those are F1: mixing of fresh groundwater and surrounding seawater (58%); F2: carbonate dissolution (18%); and F3: anthropogenic influence, i.e., nitrate contamination (8%).

In the blatinas of Mljet (Table 3), due to connection to the sea, F1 factor was significantly loaded for all analysed samples, although salinity varies from almost potable brackish water in Sobra and Blato, to almost 50% of seawater during dry season in Prožura, where F1 is strongly emphasized in any hydrological moment. In Prožurska blatina, there is also a high influence of F2 during hydrological maximum, pointing to more intense carbonate dissolution in the shallow epikarst zone during rainfall. Wells in Blato and Slatina in Kozarica have a high impact of F3 during hydrological maximum, interpreted as anthropogenic contamination, i.e., leaching of nitrates of agricultural origin by precipitation. F3 was especially emphasized as negative (with respect to initially negative variable loading) in Prožura during high groundwater levels, pointing to excessive nitrogen degradation in these hydrological circumstances. The interesting

conclusion is spatial (regional) domination of limestone dissolution (F2) and pollution (F3) during the rainy season, when washing out from the soil and epikarstic belt is present. The risk of pollution is relatively low during the dry season in the summer, and human influence on groundwater was reflected in significant slowing down of the process of ammonia volatilization during the dry season. At higher groundwater levels, this process is strongly highlighted. Highly positive values of the bipolar F3 process in Kozarica and Prožura are probably a consequence of high air temperature in the summer. In the same study [12], multivariate cluster analysis resulted with only two clusters, described as (1) marine cluster (presented by sodium and chloride ions) and (2) lithogeochemical (all other parameters). Therefore, presented factor analysis seems much more appropriate for this kind of data and gives deeper insight into this complex natural system.

5.4. Excess Sulphate Anion Content. Sulphate anion values above the limit for drinking water (Table 1) can be analysed in the context of Tables 2 and 3. It is assumed that the principal source of sulphates in Mljet aquifer is seawater, because in the geological model (Figure 2), there is no record of sulphate rocks (such as gypsum or anhydrite). Since no evaporite rocks are present on the island, it was analysed if the sulphate anion concentration is proportional to the seawater percentage in corresponding samples (Table 4). The sulphate anion concentration in seawater was adopted from [40] to be 2700 mg/l. Such analysis shows that in the case of wells in Blato, the discrepancy of measured from calculated value is -0.7%, i.e., it almost absolutely corresponds to the conservative mixing of fresh- and seawater, when measurement error and seawater chemistry variations are taken into account. However, in the case of Prožurska



FIGURE 7: Elements of Sobra desalination system (satellite imagery adopted from Google Earth), with embedded photograph of Sobranska blatina taken from the location of a desalination plant in September 2016 in the bottom-left corner.

blatina, the discrepancy was +18.7% during the hydrological minimum and -53.3% during the maximum.

For the purpose of the mentioned factor analysis, equations of linear correlation with corresponding coefficients of correlation for various measured parameters were calculated for the sample set from multiple Adriatic karst islands. The authors have determined a correlation factor of $r = 0.91$ between sulphate and chloride anions for the equation $[SO_4^{2-}] = 13.1[Cl^-] + 16.1$ [12]. A similar result was obtained by applying that calculation (the last column of Table 4). That means that applying either literature value for seawater composition or the correlation derived from numerous Adriatic islands, it is not possible to explain the sulphate concentrations measured in Prožurska blatina by conservative mixing model. Obviously, increased ion concentrations during the dry season could be the result of excess evaporation and decreased concentrations of high precipitation during the wet season. If that were the case, the regularity would also be present with other sea-derived ions, especially chloride, which is not observed.

5.5. Temporal TDS and Precipitation Analysis. TDS, determined in [10] to have a functional relationship to chloride anion concentrations ($r = 1$), was monitored at Sobranska blatina, which provides the majority of the feed water for desalination (Figure 7).

The hydrochemical composition of water from blatinas is dependent on rainfall, both directly at the lake surface and, mostly, indirectly by infiltration into aquifers and subsequently through fresh groundwater flow. The summary TDS and precipitation data, resulting from a two-year monitoring on a daily basis, are presented graphically in Figure 8 as monthly averages.

It can be observed that maximum TDS values occur regularly in September. That is the consequence of two

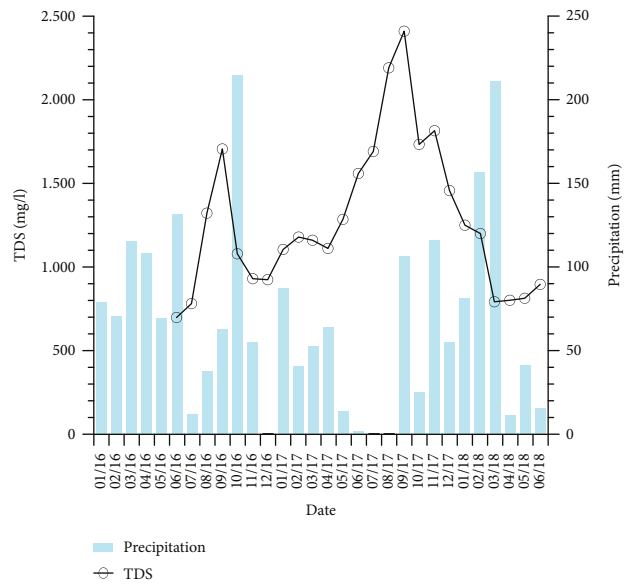


FIGURE 8: Monthly average values of TDS in Sobranska blatina and precipitation on the island of Mljet calculated from diurnal observations.

interacting factors: natural (low precipitation) and anthropogenic (increased pumping due to summer tourist season). Minimal TDS values in the Mediterranean climate area are expected after the rainy season, during the spring. However, monitoring data suggest that the lag is longer and the minimum can be expected in June (as in the cases of 2016 and 2018). In 2017 the minimum TDS was recorded in January, which is assumed to be an outlier.

However, a two-year monitoring period is far too short to determine hydrological patterns of such a complex system which is also disturbed by human activities.

What can be done is a comparison to the referent climatological period of 1981-2000 at the climatological station on Mljet. In that period, the average annual rainfall was 743 mm, with a minimum of 579 mm in 1991 and a maximum of 1099 mm in 1996. Using that as a reference, the rainfall in 2016 was 956 mm, and in 2017 it was only 562 mm. Also according to the reference climatological period, December is a month with the highest average precipitation, and in December 2016 the precipitation was zero. Extremely low rainfall can account for the fact that during 2017 with the usual pumping quantities, TDS of Sobranska blatina never fell under 1,000 mg/l.

5.6. Predicted Impact of Climate Change. According to Lang's rain factor (f), which is a quotient of annual average rainfall in mm and temperature in °C, a climate can be considered semiarid if f is in the range of 40-60, while it is arid if the factor is lower than 40 [15]. Since the average temperature in the referent period was 16.3°C, the rain factor for Mljet was 45.6, i.e., the island experiences semiarid climate, closer to arid than to semihumid part of the spectrum. In the referent 20-year period, a variability in annual precipitation is visible, with the maximum being almost twice the minimum precipitation ($\min_{1991} : \max_{1996} = 1 : 1.9$). According to the 2017 data, the minimal precipitation values display a decreasing trend.

Generally, most climate models for the Mediterranean region predict a gradual decrease in precipitation and an increase in variability, with a negative influence on water balance [41-43]. The decrease in effective infiltration into the karstified underground would obviously lead to a decrease in the groundwater levels, and one of the consequences would be an increased probability of frequent and intensive seawater intrusions.

Climate modelling for Croatian Adriatic region was conducted using five different regional climate models for the three 30-year periods during 2011-2100 and interpreted separately for northern, central, and southern parts of the Croatian coastal and insular area [44]. Results predict mean air temperature increase up to 3.5-5.5°C until the end of the century, with a swifter rise at the mainland coastal areas than on the islands. Changes in precipitation are characterized by high uncertainty, but their statistical significance increases going from present toward 2100. A drought during late spring and early summer is predicted (April-August), which will extend to September and October toward the end of the century. This trend is more significant in the southern Adriatic region. All models predicted that autumn and winter months will become slightly more humid than at present. Although weak, the prevailing trends are negative and consistent at all stations from the central to the southern Adriatic zone, thus in agreement with the drying trend observed across the Mediterranean according to IPCC [44]. If the climate data are inserted into water balance calculations, total infiltration tends to decrease significantly and by the end of the century, the water balance deficit could reach 30-47% of present values [45]. Such circumstances will probably lead to major deteriorating changes in

blatinas' hydrology and ecosystems, not to mention water supply issues. According to all climate models, extreme events such as droughts or flash floods will also become much more frequent.

6. Conclusions

Although morphology and size of the island of Mljet are not favourable for significant groundwater accumulation, its geological structure allows the formation of limited karst aquifers. Nevertheless, relatively low water demand and desalination created the possibility for local water supply. The groundwater is brackish at all extraction sites on the island and subjected to seawater intrusion in its natural state.

A combination of geological and geomorphological characteristics enables the appearance of groundwater at the surface in the form of brackish lakes (blatinas), the level of which roughly represents the water table of island karst aquifers. Blatinas are a unique natural phenomenon among Adriatic karst islands. According to presented hydrogeological conceptual model, it is possible to extract further groundwater quantities (most probably also brackish) in other parts of the island, but this should be corroborated by a multidisciplinary research program including geology, hydrogeology, hydrology, geophysics, and hydrogeochemistry.

The analysed data from diurnal monitoring of TDS at Sobranska blatina are indicative of the climatic influence to feed water composition. However, the monitoring period of two years is considered too short for an analysis of a complex karst island aquifer, additionally disturbed by seasonal anthropogenic activities. Taking into account the fact that the blatinas and karst aquifers in their vicinity represent a source of the majority of water supply on the island, it would be advisable to introduce a permanent TDS monitoring (e.g., by monitoring electrolytic conductivity using data loggers) and monthly chemical analyses, or at least two analyses annually, during hydrological minimum and maximum, at all feed water sources (blatinas and wells).

Prožurska blatina, which has the highest SP during both hydrological minimum and maximum, is not a part of the water supply system and is relatively inaccessible. Therefore, not enough data are available to derive the excess sulphate anion origin, other than seawater. Analysis of stable isotopes of sulphur from the sulphate could determine its origin as atmospheric contribution, mineral or rock contribution, marine and playa lake sources, volcanic sources, or biological contributions [46, 47].

One of the problems concerning Mljet island's water supply is an inadequate effluent management, which should be a topic of additional research. Sobra desalination plant, which is close to the coast, discharges effluent into the sea (Figure 7), but the plant in Blato discharges its effluent with an average TDS of 8,000 mg/l into the same karst polje and into Blatska blatina—its topographically lowest part. Such obviously undesirable practice has not resulted in visible negative consequences so far, which could be misleading since there is no monitoring. Effluent from RO treatment of brackish water can generally be discharged into surface water bodies if the salinity difference is less than 10% [48]. Since in

Blato the salinity difference significantly exceeds this standard, it is necessary to design a plan for treatment and sustainable effluent accommodation. If the standard is not maintained, the effluent can change the salinity of the recipient and the process can result in decreased dissolved oxygen concentrations in the water and negatively affect aquatic life [49].

This paper also tackled the question of climate changes. Climate change models predict an increase in average temperatures and precipitation variability and a decrease in effective aquifer recharge up to almost 50% by the end of this century. That suggests that the island groundwater system, which is currently operating near the maximum limit, will probably be useless if the predicted scenarios take place, especially during summer peak loads. Therefore, management plans have to be prepared for each possible scenario.

The NPKLM regional water supply system which connects Mljet to the mainland via submarine pipeline is currently being put into operation. The process will take years and presented water supply from the island's own resources will have to remain active. Even afterwards, these quantities should not be neglected and should stay operational. Water in NPKLM comes from a strong karst spring on the mainland, with minimal discharges of $3 \text{ m}^3/\text{s}$ and maximal above $10 \text{ m}^3/\text{s}$. Quantities used for water supply are approximately ten times lower than minimal discharges, so the supply can be considered secure. Still, this water has slightly increased sulphate anion concentrations as a result of the dissolution of gypsum and anhydrite rocks in its catchment area outside of the Croatian territory. Trans-boundary management of this large karst catchment area is still being established and is a topic of hydrogeological and geological investigations.

In the context of observed behaviour of the hydrogeological system of the island of Mljet and the predictions for both the narrower Adriatic and wider Mediterranean region, long-term sustainable water supply must be ensured taking into account the water demand, existing desalination practices, and connection of water supply system to the mainland, as well as the water availability in the context of climate change.

Data Availability

Data procured as described in "Materials and Methods" section which is not directly presented in the paper is public domain and can be procured from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

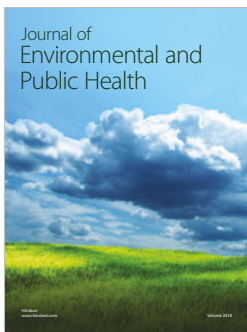
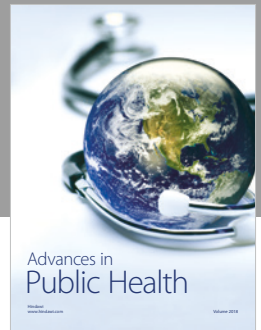
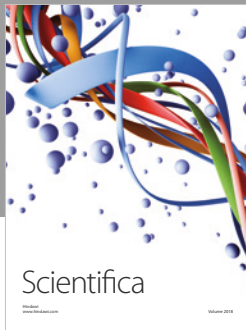
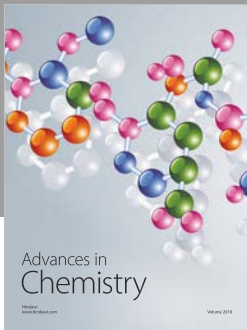
The authors would like to thank Tamara Marković from the Croatian Geological Survey for performing hydrochemical

analyses, as well as to the Croatian Meteorological and Hydrological Service for the preparation and swift delivery of the data. Furthermore, the authors are very grateful to the former and current directors of the water supply company "Voda Mljet," Ivan Sršen and Petar Benković, for granting them access to company data and facilities and to Drago Hajdić from their technical service, who helped with fieldwork, sampling, and overall logistics. This research was carried out within the framework of the research project "Basic hydrogeological map of Croatia," funded by the Croatian Geological Survey.

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