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Influence of water levels of Vrana Lake and the Adriatic Sea to the water chemistry of Vrana lake

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The set objective of this field research was the determination of anomalous states in the Vrana Lake waters that might be the consequence of environmental pressure. We postulated that water quality in Vrana Lake Nature Park would be mainly influenced by the agriculture and impact of the sea and climate. Methods employed include analysis of dynamics of temperature and precipitation, sea water and lake water levels and water monitoring in a time period from January 2000 to December 2009. Adriatic Sea and Vrana Lake water levels were monitored at water gauges placed at two sites. Water sampling was carried out at two measuring points as a part of the national water monitoring program. Comparison of water fluctuation levels in the lake and the sea with concentration dynamics of calcium, magnesium, chloride and sulfate ions, reveals that the relationship between lake water levels and sea water levels has a powerful and direct impact on the chemical activity of the lake water. The alkalinity and high electro conductivity of lake water is the consequence of mixing process with seawater. Penetration of sea water into the lake corresponds with the duration and intensity of the dry periods. Data on lake water hardness in location Prosika follows the same trend as data regarding ions and electro conductivity at the same location. Since our data indicates that with the change in the lake water and the sea water levels, the salinity of the lake changes, we conclude that sea water is the major source of salt in the lake.

Key words: influence of water levels, Vrana Lake, Adriatic Sea, lake water chemistry

INTRODUCTION

Some of the latest protected areas in Croatia is Vrana Lake Nature Park – established in 1999. Tender age of this nature park is most likely the reason why this area has not been systematically studied in the context of sustainability (BARROW, 2006) and area protection (MARTINIĆ, 2010). Vrana Lake Nature Park is situated north-east from Pakoštane in Zadar County, and is part of the Vrana basin, which contains several plains and the lake. Vransko plain together with Vrana lake is commonly described as Vrana basin. Vrana basin, which encompasses Vrana lake, covers the area of 5.745,69 ha (MARKOVIĆ, 2010), which is in the Vrana Lake Nature Park protection act rounded to 57 km^2 (OG, 77/99), and includes complete Vrana lake watershed. Vrana lake is the largest lake in Croatia and is located in the south-east part of land depression running along Dinaric Alps. Vrana lake is under specific influence of the Adriatic sea, where two are connected via Prosika canal made in 1770 (MLINARIĆ, 2009). Vrana lake is an important economic resource to the local community but also a habitat for numerous bird species (TUTIŠ & RADOVIĆ, 2003). So far research has been conducted on water quality, phyto-isoplankton, macrozoobenthos, habitat types and inventory of flora, ichthyofauna and fauna (MRAKOVČIĆ *et al.,* 2003, 2004). To this day, more research has been done on land than on water topics. ROMIĆ (1994) investigated effects of salt water on the soil and looked into possibility of using Vrana Lake waters for agricultural land irrigation. ROMIĆ *et al.* (2009) looked into soil quality in Vrana Lake watershed. Systematic ornithofauna monitoring (RADOVIĆ *et al.,* 2004) is conducted by Institute of Ornithology of Croatian Academy of Sciences and Arts. Because of the specific hydro-geological circumstances (ŠVONJA, 2003) and Prosika canal, Adriatic Sea waters can enter the lake, making Vrana Lake water unsuitable for agricultural irrigation. Irrigation with such salty and alkaline waters from Vrana Lake is long-term unsustainable (ROMIĆ 1994, 1995). Such practice could leave lasting consequences on soils in terms of alkalizing adsorption complex, salt concentration increase in the soil colloid, as well as increased mobility of harmful substances such as cadmium (MA & RAO, 1997). Purpose of this paper is to establish connection between lake waters with climate influences and Adriatic Sea waters penetration.

MATERIALS AND METHODS

Water sampling

As a part of the state-wide surface water monitoring program, conducted by Hrvatske Vode, in the area of Vrana Lake Nature Park, two monitoring locations have been established (Fig. 1). Sampling is done once a month. Monitoring station Vrana lake Motel, is located in a vicinity of Kotarka river estuary, close to Crkvine camp. Prosika monitoring station is located at the opposite side of the lake, by Prosika canal.

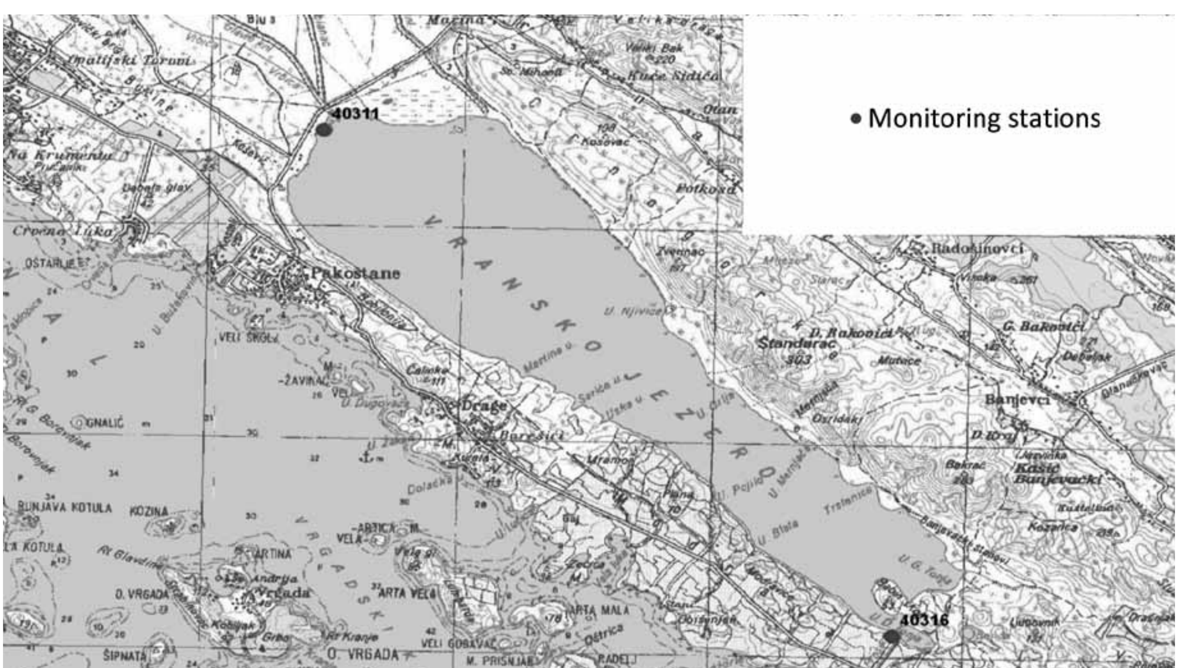

Fig. 1. Water quality monitoring stations: 40311: Motel; 40316: Prosika canal (Hrvatske Vode, 2009: Vrana lake water quality monitoring 2000-2009, internal document)

Data used in our research was collected from January 2000 to December 2009.

Water level measurements

Water level monitoring on Vrana lake is conducted by Hrvatske Vode. Measurements are taken at 7 locations. Samples are taken every day at 13.00. For this project, data was collected at two locations in the period of 2000-2009:

- monitoring station at Prosika canal entrance (with modern water gauge, reflecting very reliably water level in the lake;
- sea water level gauge, on the sea side of the Prosika canal.

Measuring stations at Vrana lake belong to "Supplementary stations" class, and data is property of Hrvatske Vode and Meteorological and Hydrological Service (DHMZ). Measuring station PROSIKA - VRANSKO JEZERO (Prosika–Vrana Lake) was established in 1946 but monitoring began on 01th of January 1948 on one-piece vertical water gauge calibrated from 0-200 cm, which was located at the mouth of Prosika canal which serves for release of lake water into Adriatic Sea. Water level gauge at Prosika is at 0,057 m below sea level, therefore to all measured data we had to deduct 57 mm to get an accurate water level in the lake. Coordinates for this water gauge are: X=4 856 374; Y=5 550 969. Measuring station PROSIKA-JADRANSKO MORE (Prosika–Adriatic Sea), was established on 01th of November 1986. Limnigraph type SEBA-Delta was installed on 01th of January 1989 and in 2003, replaced with electronic type OTT–Thalimedes. Zero point is at 0,002 m above seas level, therefore all measurements have 2 mm added to their respective values. Coordinates for this level gauge are: X=4 855 701; Y=5 550 434. It is important to note that on 26thof August 2009 threshold in the canal was raised for 45 cm, which has a direct influence on maximum lake water levels and on sea water penetration in the lake.

Climatic parameters measurements

To establish inter-relationship with lake water levels, DHMZ furnished us with median daily air temperatures and daily rainfall data for the period 2000-2009, collected at the meteorological station Biograd na moru. Data is structured to establish a correlation with lake water levels, and for graphical interpretation.

Statistical data processing and interpretation

For every data point and every location statistical analysis was conducted on a basis of data collected for every year, 12 data points per year. Statistica 8 (StatSoft, 2008) was used for statistical data analysis. Descriptive statistics was used to determine minimum and maximum, arithmetic mean, median, correlation coefficient, standard deviation, asymmetric coefficient g_1 (skewness). Frequency distribution is shown graphically. In case of strong asymmetric data distribution (g_1>1) logarithmic transformation was applied to normalize distribution before statistical processing.

RESULTS AND DISCUSSION

Chemical properties of Vrana lake waters

Acidity

According to measured values of pH, Vrana Lake water is mildly alkaline. The pH values of the surface water, during observation period, varied between 6,7 and 8,8. Measured values are within borderline values assigned to class I waters (OG, 77/1998). Water alkalinity on both locations varied during observation period. In larger number of cases, water at Prosika canal was always more alkaline. Correlation between two data sets, one from each location, is relatively low (r=0,62), which can be attributed to different factors responsible for pH values of the lake, especially to the Adriatic sea at canal Prosika.

Electro conductivity

Correlation between salt concentrations measured at locations Motel and Prosike is relatively strong (r=0,92). From 2000 do 2007 EC_w

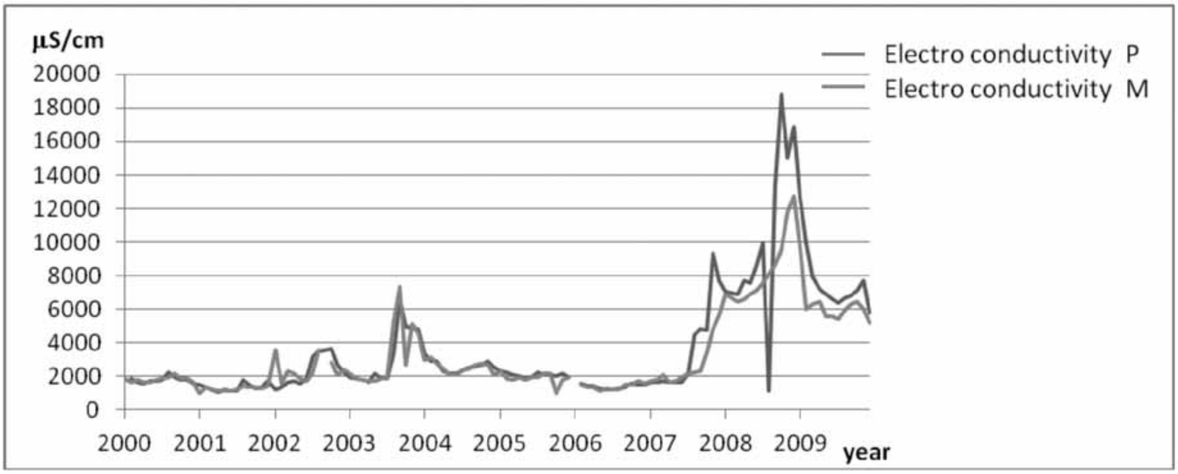

Fig. 2. Lake water electro conductivity dynamics (ECw) (P - Prosika, M - motel)

values at both localities are between 1.000 and 3.000 µS/cm, with an extreme values being registered in the second half of 2003 (up to 7.000 µS/cm). Extremely high values were detected in 2007 and 2008 with values starting to dropp in 2009 (Fig. 2). It is indicative that Prosika values are substantially larger than those obtained at Motel (Prosika max. values are ~18.000, and those at Motel are 13.000 µS/cm). Very similar electro conductivity values at the north-west side of the lake obtained ROMIĆ (1994) in the period of 1988-1992. This anomaly is well explained by water level fluctuations during 2007, 2008 and 2009. Namely, during 2007 and 2008 water levels did not follow normal pattern. Lake water levels were mostly below sea level (second half of 2007 and most of 2008), causing Adriatic Sea water to penetrate (via tidal waves through Prosika canal) into the lake. Only in 2009 normal lake water levels were restored, meaning lake water drained into the sea via canal. Lake water level became higher, which was helped by adding 45 cm threshold to the canal. The consequence was that during 2009 because of increased lake water level and absence of sea water spillover through Prosika canal gradual lowering of salt concentration in the lake occurred. Hence, 2007 is known as salinization year and 2009 as desalinization year. This regularity in the change of electro conductivity was confirmed by measurements of ROMIĆ (1994), with difference that in our case we have data from two measuring stations. During "regular" years, from 2000-2006, there is no difference in salt concentrations between locations, while during years of the low water levels and during sea water influx in the lake, 2007–2009, salt concentration were significantly higher at Prosika location.

Hardness

Total lake water hardness, as expected, often correlates with electroconductivity. Typical values are between 300 and 500 mg CaCO3/L (LOWER, 1999), which are values higher then average for crass waters (around 205 mg CaC03/L). In 2007 there was noticeable increase in water harness which persisted during 2008, but dropped in 2009 (Fig. 3). During that period lake water hardness at Prosika was significantly higher than at Motel although correlation between measured values of this parameter between two locations is relatively strong (r=0,91). This anomaly is understandable when we take into account influence of low water level and influx of sea water on the increase of salt concentration in lake water. This is primarily referring to chlorides which contribute to water hardness, especially at Prosika location (over 2000 mg/L).

Calcium ions

Calcium concentration in lake water is usually between 50 and 150 mg/L, expect during 2008 and 2009, when it reached values up to 250

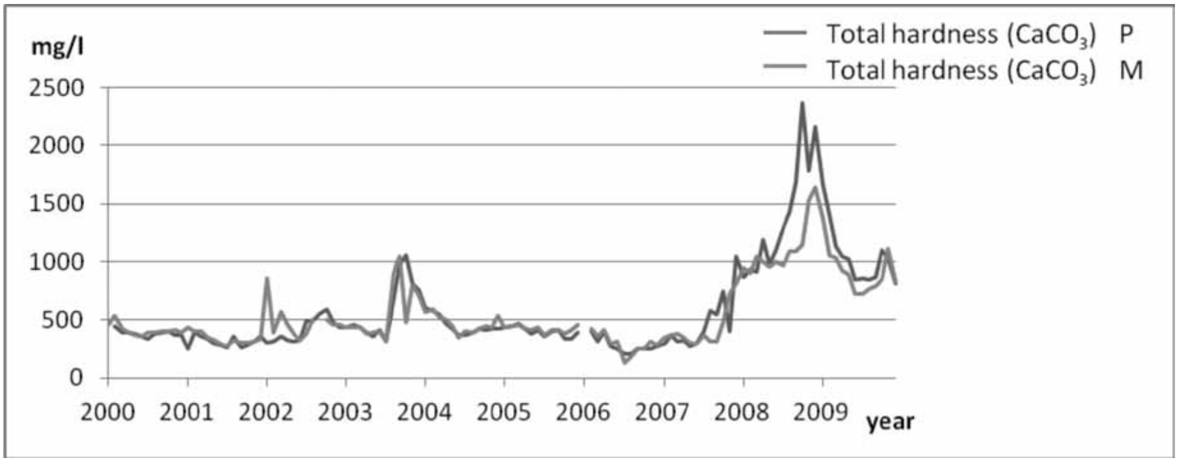

Fig. 3. Total hardness dynamics of the lake water (P - Prosika, M - motel)

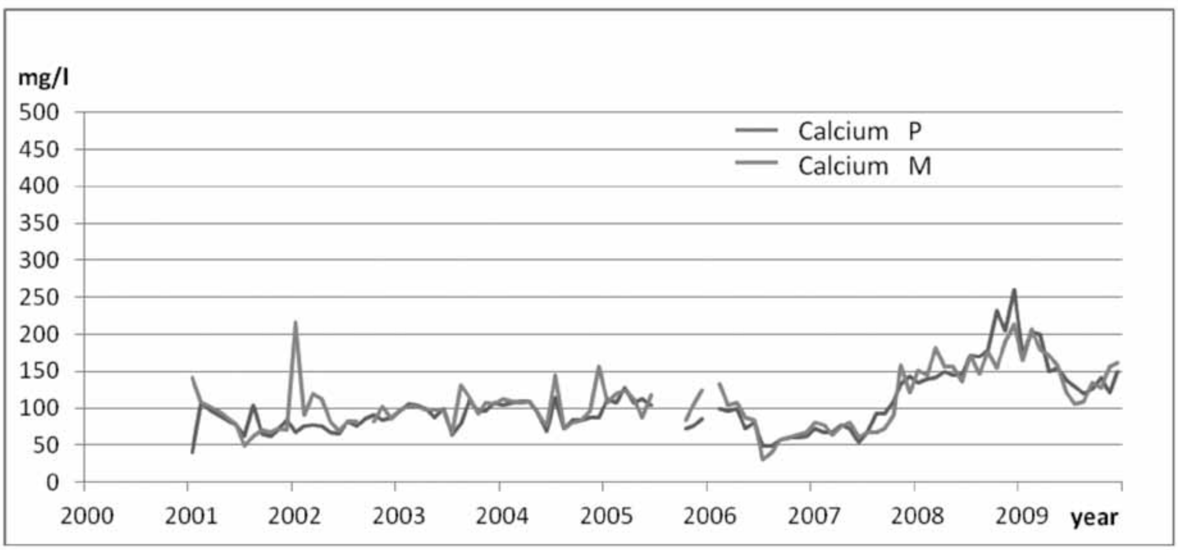

Fig. 4. Ca^{2+} concentration dynamics in the waters of Vrana lake (P - Prosika, M - motel)

mg/L. These extreme values are coincidental with the drought during 2008, and with second half of two-year low water level period in the lake and with penetration of the sea water in the lake (Fig. 4). Values have high correlation coefficient at both locations (r=0,79).

Magnesium ions

Magnesium concentration in lake water is between 25 and 50 mg/l, and sometimes there are concentration spikes up to 430 mg/l (Fig. 5). Unlike concentration of calcium ion, which is equal at both locations, average concentration of magnesium ion is somewhat larger at Prosika, which is connected with influence of sea water (sea water contains more magnesium then calcium). Besides, extreme values of magnesium ion are far more pronounced from maximum values of calcium ion, especially at Prosika, and values for both locations have even stronger correlation coefficient (r=0,89). These values correspond with long drought in 2008, and are strongly related to sea water penetration in the lake during 2003, 2007, 2008 and 2009.

Chlorides

Chloride ion concentrations in Vrana lake correspond to concentration changes of calcium and especially magnesium ions as well as to sea water influx after long periods of no rain.

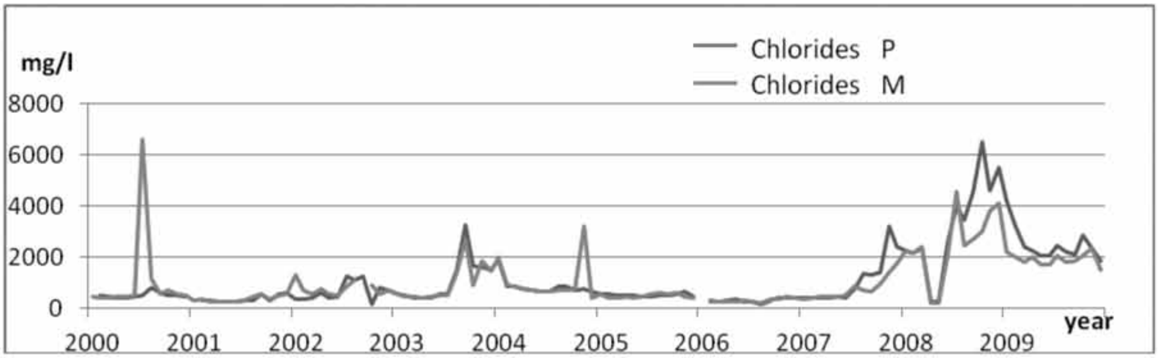

Fig. 6. Cl$^-$ ion concentration dynamics in Vrana lake vater (P - Prosika, M - motel)

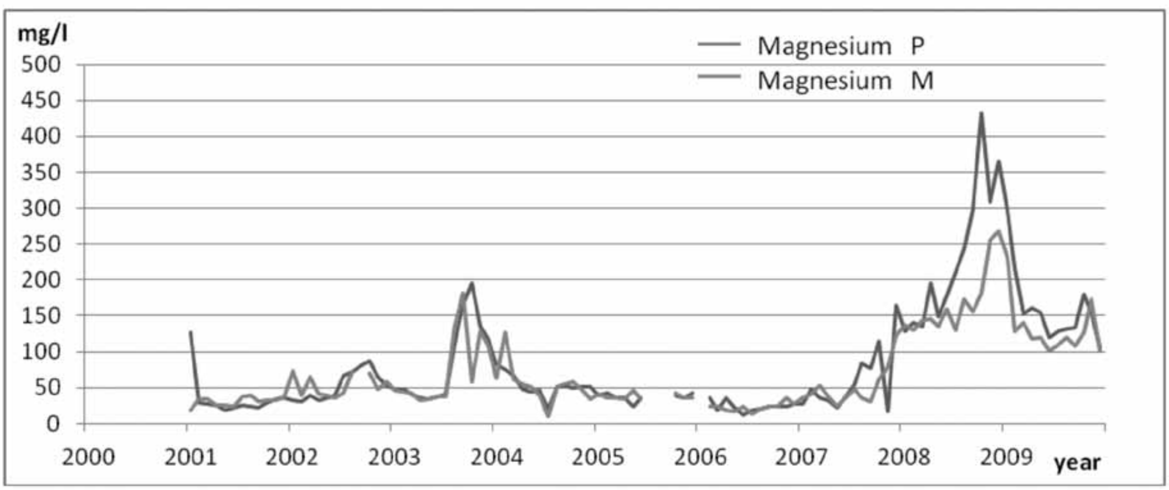

Fig. 5. Mg^{2+} ion concentration fluctuations in waters of Vrana lake as measured at two locations (P - Prosika, M - motel)

This connection is evident from strong correlation coefficients (r=0,91 for Prosika and r=0,83 for Motel). Lower correlation coefficient at Motel location is a result of anomalies stemming from high chloride concentration in 2000 (one sample) and 2004 (one sample).

When we leave out extreme values, which are mainly connected with long drought periods, chloride concentration in lake water is mainly in the range of 200-800 mg/l. Extremely high values can reach over 6.000 mg/l and are regularly higher at Prosika (Fig. 6). Magnesium, chloride and calcium ion fluctuations are excellent proxies for electro conductivity.

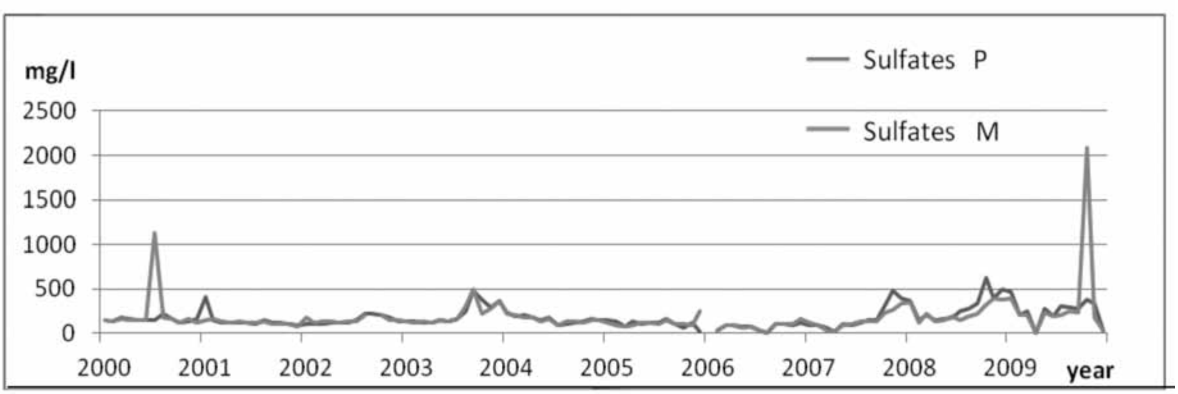

Fig. 7. SO$_4^{2-}$ ion concentration dynamics in Vrana lake vater (P - Prosika, M - motel)

Sulfates

Concentration of sulfates in lake water is mainly in the range between 100 and 500 mg/L.

On two occasions, spikes have been recorded at Motel locations, which were not connected with any known causes. Sulfates concentration dynamics corresponds with changes in concentration of magnesium and chlorides in the lake water, and with influxes of sea water in the lake (Fig. 7).

Temperature and precipitation dynamics at meteorological station Biograd na moru

Air temperature and precipitations are essential factors for water regiment of any area. For comprehensive overview of the climate, 20 year data from meteorological station Biograd na Moru were used. For water monitoring in Vrana basin, data from 2000-2009 were used. Average daily air temperature in the above-mentioned period is showing characteristic oscillations. Notable exceptions are minimum values for winter temperatures in 2000/2001, 2006/2007, 2007/2008 and 2008/2009. This anomaly is also showing in average monthly air temperatures for these months with temperatures higher than average. As for yearly averages, 2005 is an exception, when yearly average was 14,3°C. In ten year cycle, yearly averages are between 14,3°C and 15,7°C, but when we observe ten year average (15,3°C), it is higher for 0,5°C in comparison to previous twenty year (1981–2000) period (14,8°C). If we look at precipitation data in a ten year cycle, we observe two exceptions among precipitation yearly averages. Significantly lower averages were recorded in 2001 (691 mm), 2003 (559 mm), 2006 (649 mm), 2007 (499 mm) and 2008 (625 mm). Years 2001 and 2003 are at the levels of twenty year average (1981-2000). Highest averages are in 2004 (1020 mm), 2005 (1117 mm) and 2009 (1078 mm). Such distribution of precipitation averages indicates that 2003, 2006, 2007 and 2008 were extremely dry years, which is reflected in the soil moisture content, lake water level, and subsequently in lake water quality. This interpretation can be false unless we take into account annual precipitation distribution and correlation of precipitation values and temperature values. For example, 2003, 2007 and 2008 had extremely dry summers. Extremely dry winters were in 2001/2002, 2006/2007, and 2007/2008. Driest year was 2008 due to cumulative effect of two-year drought (2007, 2008). Total ten-year period, according to precipitation average, has 3% less precipitation then previous twenty-year period. Droughts are lot easier to explain using synergy of precipitation and temperatures with Lang's rain factor (for 1981-2000 period its value is 55). Its range, for a ten-year cycle is between 32 and 78 and according to it, driest year was 2007, and wettest year was 2005. Furthermore, when we analyze fluctuations of monthly R-factor (GRAČANIN, 1947), which reflects synergy between temperature and precipitation during a year, than we see that during some years, winter months had arid character (especially year 2006/2007).

Sea and lake water level dynamics

Strong influence of Adriatic Sea to Vrana basin is manifested by the sea water penetration through calcareous flysch barrier and through man made canal Prosika. Lake water levels are mainly determined by level of precipitation (waters arriving into the lake via watershed drainage) as well as evaporation. According to FRITZ (1984), Vrana Lake receives yearly 60-120 mil. m^3 of water. From lake, water is drained off via Prosika canal into the Adriatic Sea and is also lost via transpiration. BERAKOVIĆ (1983) determined that from the lake surface (30 km^2) 49,5 mil. m^3 of water is lost via transpiration. Lake and sea water levels were measured on both sides of Prosika canal; on one side sea water levels and on the other side lake water levels. Measurements were taken daily, from 2000 until the end of 2009. Collected values are indicating typical fluctuations of the lake water levels, which have its maximum during winter-spring period and its minimum during summer-autumn period (Fig. 8). Lowest levels are recorded from August until October, which

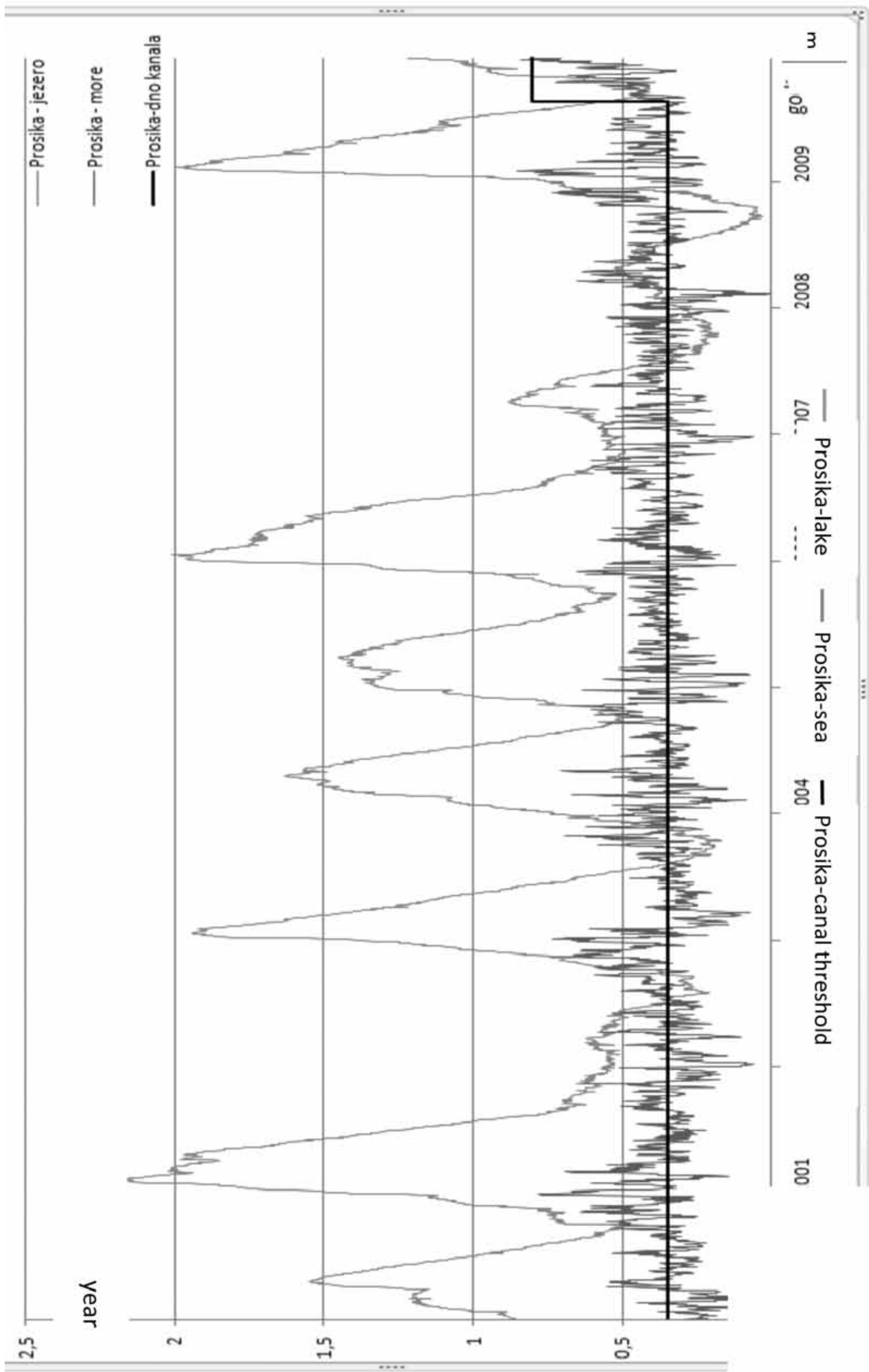

Fig.8. Lake and sea water level fluctuation as measured at opposite sides of Prosika canal with respect to the canal threshold (that was raised for 45 cm in from 26.08.2009)

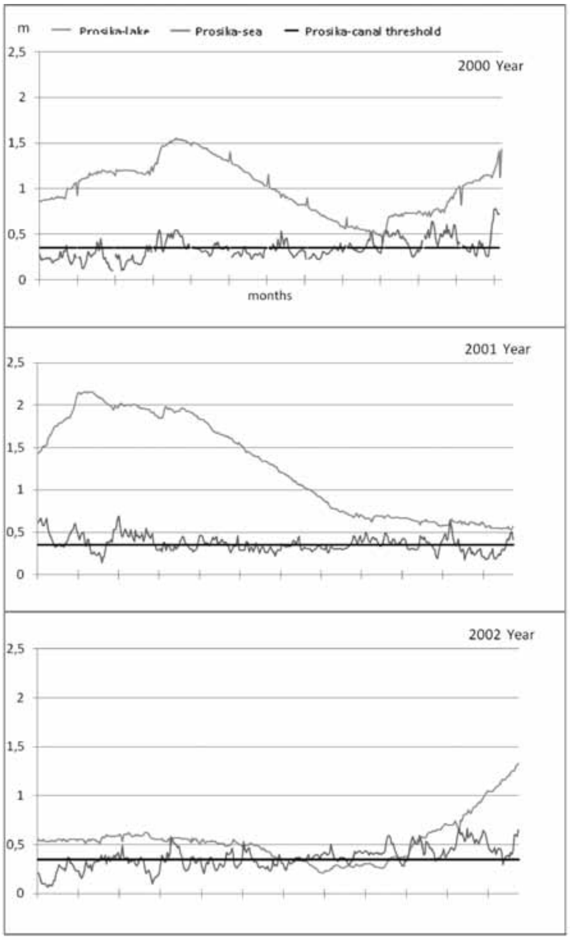

Fig. 9. Lake and sea water level fluctuation from the 2000 to 2002 Year

confirms findings by ROMIĆ (1994). Anomalies are present during long summer dry periods, when (due low precipitation, reduced watershed drainage and increased transpiration from lake surface), we detected drop in or stagnation of lake water level. Result of that is that sea water surges into the lake via Prosika canal (Fig. 8). Contact between sea and lake is not only through Prosika canal but also via calcareous dolomite flysch barrier. Spill over of sea water through Prosika canal happens when sea water level is higher than bottom of the canal and lake water level (Fig. 8). During 2000, 2001, 2004, 2005, 2006 and 2009 these incidents did not occur because lake water level was above sea water level. In 2009 these incidents were prevented by adding 45 cm to the canal threshold. Largest sea water penetration was recorded during driest periods in 2007 and 2008, when lowest air temperature averages and lowest total precipitation averages were recorded. That was especially evident in the fall of 2007 after extremely dry summer. In 2008 cumulative effect was evident (despite larger precipitation in the spring time), and sea water penetration through Prosika canal was undergoing throughout the whole year. Significant penetration was also recorded in the fall of 2003 (Fig. 10), when the driest summer in a decade was recorded (lowest precipitation and highest temperatures). Another significant spill over was also recorded in the summer of 2002, evidently as a consequence of very dry second part of 2001 and first part of 2002 (Fig. 9).

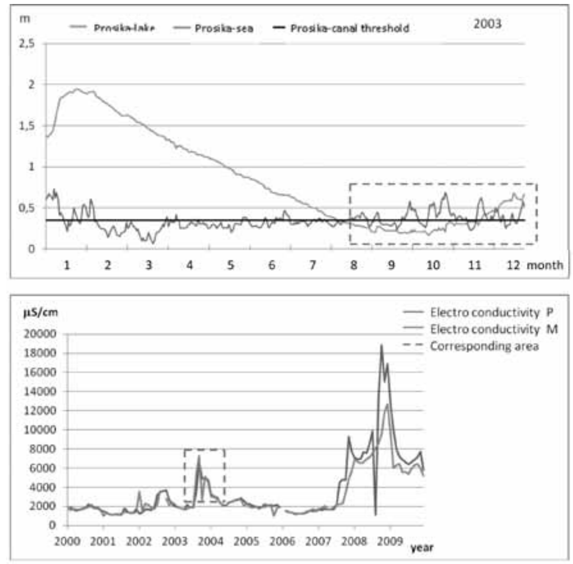

Fig. 10. Corresponding sea water penetration with electro conductivity

Fluctuations of sea level were reported as daily averages to compensate for ebbs and tides. Fluctuations are strongest during cold periods of the year and weakest during the warm periods of the year. In the period of 2000-2009 maximum lake water level difference was 2,13 m. Maximum yearly average fluctuation was measured in 2001, and it was 1,7 m (Fig. 9). During investigation period minimum yearly fluctuation was measured in 2007, when it reached the lowest water level of the lake (0.03 m) and is 0.5 m. Sea water penetration via Prosika canal corresponds with electro conductivity (Fig. 10) and water hardness data, and fluctuations in calcium, magnesium and chloride ion concentrations.

DISCUSSION

Previous work (BELLA, 1935) has determined that Adriatic Sea water communicates with Vrana Lake waters. Besides intensive communication that takes place through Prosika canal, which in its nature is anthropogenic, there is natural communication that is taking place through two flysch barriers north of Biograd, and through karst reef around Prosika (KAPELJ *et al.,* 2003). Reef that is up to 1,5 km in width separates Vrana Lake from the sea. Geological mapping in two areas was done by FRITZ (1984) taking into account geological lack of homogeneity of the reef, which is causing different permeability in different areas of the reef. Daily lake water level measurements (HALL, 2003) during any of the observed years reflects maximum during winter-spring period and minimum during winter-fall period. Data suggests that during dry periods minimum lake water levels are so low that sea waters enter the lake. Apart from amount of precipitation, tidal waves also play role in water level difference between sea and the lake. We determined that average daily sea level can, depending on the precipitation on the lake side, and tidal waves on the sea side, be higher than Vrana Lake waters or be below their level. In the cases of the higher sea water level, higher hydrostatic pressure pushes sea water through porous karst rocks. In the cases of the extreme sea water levels, sea water passes through Prosika canal into the lake. In those circumstances significant overflow of the sea water in Vrana Lake can happen, making lake water brackish (MIŠETIĆ & MRAKOVČIĆ, 2003). This was documented during several months in the years with very little precipitation (2003, 2007, 2008). On the other hand, lake water levels were higher than the sea level during rainy years (2000–2002, 2004–2006, 2009). This resulted in the drain of lake water into the sea (Fig. 9). Our data confirms previously published results (ROMIĆ, 1994), whose data pertain to period of 1988-1992. Changes of water levels between the sea and the lake are showing that those water levels are mutually independent. There is no correlation between them over log period of time. Comparison of water levels in the lake and the sea with ion concentrations (calcium, magnesium, chloride, and sulfate ions) shows that water level ratio has strong and direct influence on the lake water chemistry. Low lake water levels in the fall are the result of reduced precipitation and higher evaporation rate. In those periods if lake water level drops below Prosika canal threshold, sea water enters the lake, and ion concentrations increases several fold. Same observation was noted during water electro conductivity measurements. Lake water hardness data (collected at Prosika) follow the same trend as ion concentrations and electro conductivity data. Based on water level data and ion concentration in the lake, we conclude that sea water is main source of salts in the lake. Observed changes in hydrological patterns in the wider area are connected with increased arid character of the area. During monitoring period of 10 years (2000–2009), three years could be considered extreme (2003, 2007, 2008). It is expected that hydrostatic pressure as a main driver of sea water infiltration in to the Vrana Lake increases. Especially now that increased threshold at Prosika canal will reduce overflow incidents.

CONCLUSIONS

High values of electro conductivity of Vrana Lake waters are the result of sea water penetration through calcareous flysch barrier, as well as through Prosika canal. Comparison of water levels in the lake and the sea with ion concentrations (calcium, magnesium, chloride, and sulfate ions) shows that water levels ratio has strong and direct influence on the lake chemistry. Infiltration of sea water in the lake is in direct connection with long term dry periods. Ten-year precipitation and temperatures data gathering at meteorological station Biograd has shown increased arid character of the area (in comparison to the previous decade) directly influencing water conditions of the Vrana basin.

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Utjecaj razina vode Vranskog jezera i Jadranskog mora na kemizam vode Vranskog jezera

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SAŽETAK

Kao cilj istraživanja na terenu postavljena je determinacija anomalnih stanja u vodi Parka prirode Vransko jezero koja bi mogla biti posljedica pritisaka na okoliš. Očekuje se da pritisci na kakvoću vode Vranskog jezera dolaze od poljoprivrede u slivnom području, ali i utjecajem mora i klime. Metode uključuju analizu dinamike temperatura i oborina i dinamika razine morske i jezerske vode za razdoblje promatranja od siječnja 2000. do prosinca 2009. Dinamika razina mora i jezerske vode praćena je na vodokazima postavljenim na dvije lokacije. Uzorkovanje vode provedeno je na dvije mjerne točke u sklopu državnog praćenja stanja voda. Usporedbom dinamike razine vode u jezeru i razine mora s dinamikom koncentracije iona kalcija, magnezija, klora, te sulfatnog iona, vidljivo je da odnos razine vode u jezeru i razine mora ima direktan i snažan utjecaj na kemizam jezerske vode. Lužnatost i njena visoka električna vodljivost posljedica su miješanja s morskom vodom. Činjenica da se promjenom odnosa razine jezerske vode i razine mora mijenja i koncentracija soli u jezeru pokazuje da je morska voda izvor soli u jezeru. Prodor morske vode u jezero korespondira s dugotrajnošću i izraženošću sušnih razdoblja. Podatci o tvrdoći jezerske vode na Prosiki prate isti trend kao i podatci o ionima i električnoj vodljivosti. Činjenica da se promjenom odnosa razine jezerske vode i razine mora mijenja i koncentracija soli u jezeru pokazuje da je morska voda izvor soli u jezeru.

Ključne riječi: utjecaj razina vode, Vransko jezero, Jadransko more, kemizam jezerske vode