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Monitoring of Water Salinity of the Lower River Neretva (B&H)

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Abstract: Water regime in the lower course of the Neretva River (Bosnia and Herzegovina) is very complex because of the downstream side impact and built hydropower system with the upstream side. Sea inflow into the aquifer and the surface flows of the valley depends on the amount of flow of fresh water from the basin. In the dry season, when inflows from the catchment reduced and longer duration, can not be drawn into the bed of the river in the form of salt 'wedge', and in the aquifer rises from deeper layers to the surface. This phenomenon extends deep upstream in the river valley. By measuring the physical (salinity, temperature, electrical conductivity) and chemical (amount of dissolved oxygen in water and pH) parameters at lower flow of the river Neretva (delta) water quality was determined with special attention to the occurrence of salinity. During the one-year monitoring were conducted field tests of physical-chemical parameters of the lower course of the Neretva river at 20 locations of significant testing maritime impacts on water quality. The physical parameters were measured temperature, conductivity and salinity, and the chemical quantity of dissolved oxygen, expressed as a percentage and mg L^{-1} in water and the pH value. The values of the above parameters were measured on the fild with combined meter WTW Multi-Parameter Instruments.

Keywords: Salinity, Sea Impact, Water Quality River NERETVA (B&H)

1. Introduction

The Neretva River is the largest river of the Adriatic catchment area. It flows 203 km through Bosnia and Herzegovina, and the last 22 km through the Croatia. Water regime in the lower course of the Neretva River is very complex because of the downstream side impact and built hydropower system with the upstream side. Sea inflow into the aquifer and the surface flows of the valley depends on the amount of flow of fresh water from the basin. In the dry season, when inflows from the catchment reduced and longer duration, cannot be drawn into the bed of the river in the form of salt 'wedge', and in the aquifer rises from deeper layers to the surface. This phenomenon extends deep upstream in the river valley. Neretva plains expanding into the largest alluvial delta of the Adriatic area of 24,585 ha of which 12,000 ha are in Croatia and the rest in Bosnia and Herzegovina. Upper Herzegovina part of the delta, with an area of 7,411 hectares, the wetland is an area called Hutovo Blato [1].

Apart from the natural effect of the quality of water systems, the situation is exacerbated by human activity. Mainly, quality of surface water is under constant influence of the sediment substrate, and largely influenced by climatic factors (temperature and rainfall) [2].

Water regime in the lower course of the Neretva River is very complex because of the impact of the downstream side and built hydroelectric system with the upstream side, in particular HE Mostar and HE Svitava power plants. All of that influence to the quality of water of Lower Neretva. On the one hand, multi-year reduction of groundwater inflow of fresh water from the river Trebišnjica and uncontrolled deepening of the riverbed of the Neretva River, and on the other sea-level rise due to global warming, leading to an increase in the salinity of water Neretva basin [3].

Salty water constantly penetrates into underground waterways leading to the salinity of the soil and the reduction of arable land intended for intensive planting vegetable crops, as well as continuous pumping of large quantities of water from underground [4].

In the dry season, when the reduced inflow of the basin and of longer duration, not retractable into the river in the form of the salt 'wedge', and the aquifer is raised from the deep layers of the ground surface. This phenomenon extends deep upstream in the river valley. Intrusion into the aquifer and into surface water valleys depends on the amount of fresh water inflow from the catchment [5].

Measuring the physical (temperature, conductivity - CND, total dissolved salts - TDS) and chemical (dissolved oxygen content, expressed in percentage, and mg L-1 in water, and pH) parameters on the 20 locations of significant test of the maritime influence on the quality of the water was the aim of this study. The values of these parameters are measured on the field combined meter WTW Multi-Parameter Instruments. Special attention is given appears salinity.

Salinity is expressed as a fraction of dissolved salt per thousand parts of water (ppt - parts per thousand = g / kg = ‰). High salinity contributes sodium and chloride ions, the ingredients sodium chloride known as common salt. Bays and river mouths are of a very wide range of salinity, because in these places there is a mixing of fresh and salt water. The salt content in the water is one of the important factors in advance and indicate which groups of organisms can be found in water [6].

This study can also provide a proposal for future research and protection of that area.

2. Materials and Methods

For the purpose of sampling and research were selected twenty (20) location of important testing maritime impact on water quality [7]. Selected locations range from Žitomislić on the North to Gabela on the South, including Trebižat in the West and Deransko lake in the East. Altitude range is from 0.00 m (Deransko lake and Krupa) to 32,5 m (Bivolje Polje).

The values of all parameters were measured on the ground with combined meter WTW Multi-Parameter Instruments. Measurements were carried out at six dates during a year on the field at all locations. Six outings on the field covered four seasons and the highest a lowest water level.

Physico-chemical analyses were carried out using standard methods [8]. Accuracy of each method is prescribed by the APHA methodology. The device has three separate electrodes intended for measuring these parameters. Each of them can measure temperature of water.

Measuring range for electrical conductivity CND is from 1 μScm^{-1} to 2 μScm^{-1} (at temperature range of -5°C to 80°C). The unit for measuring salinity is practical salinity units PSU (Practical Salinity Unit). Total dissolved solids (TDS) measuring range of 0 mg L^{-1} to 1999 mg L^{-1} for a temperature range of -5°C to 80°C. Dissolved oxygen was measured by the oxygen electrode. The values are in mg L^{-1}. Oxygen saturation was measured in the same manner, and the displayed value is expressed in percentage (% O_2). pH was measured by pH electrode device WTW multi-parameter Instruments.

The data were processed using methods of descriptive statistics. The studied parameters are described numeric values: range or difference between the maximum and minimum values; medium or average values; standard deviation or deviations from the mean values and coefficient of variation.

In order to establish the existence of certain causal relationships among the studied parameters made their comparison using the correlation established a connection is numerically expressed by Pearson correlation coefficient.

Statistical analysis was performed using the tools Microsoft Excel for statistical analysis. Pearson correlation and descriptive statistics were performed.

3. Results

Water temperatures were in the range ± 24.5°C and low temperatures of 4.3°C to a maximum of 28.8°C (Table 1).

Table 1. *Monitoring of water temperature.*

Location	Water temperature (°C)					
	September 2015.	**January 2016.**	**March 2016.**	**May 2016.**	**June 2016.**	**July 2016.**
Ada Čapljina	14,5	8,3	10,4	11,5	12,8	17,2
Bjelave Čapljina	19,3	8,3	10,2	11,3	12,7	17
Trebižat	14,6	10,4	12,4	13,6	15,5	17,6
Čeljevo	15,2	8,7	10,6	11,5	14,4	17,6
Gabela	15,7	8,9	10,6	11,2	14,7	17,6
Svitava I	21,6	8,9	11,1	17,2	23,2	28,8*
Svitava II	16,4	6,3	14	13,9	16,8	19,6
Višići-rukavac	19,1	10,5	12,3	12,1	12,9	18
Deransko lake I	18,5	5,5	12,2	15,7	19,3	23
Deransko lake II	22,4	6,5	12,1	15,7	20,2	23,3
Krupa	16	4,3*	12,1	15,7	20,1	21,5
Karaotok	17,5	4,7	12,3	15,6	20,3	20,6
Škrka I	17,7	6,1	12,5	13,9	18,6	22,6
Škrka II	16,9	12,5	13,3	14,2	18,3	24,5
Klepci	17	8,5	10,9	11,9	14,2	17,7
Bregava	17,1	10,4	12,1	12,5	15,2	17,8
Počitelj	17,1	8,5	10,3	11,1	13,6	17,4
Ševaš Polje	15,9	8,3	10,2	11,2	13,4	17,5
Bivolje Polje	15,5	8,3	10	11,2	13,3	17,3
Žitomislić	15,6	8,5	9,9	12,3	13,7	17,2

* max and min value

January water temperatures were in the range of ± 8.20°C. The lowest temperature (4.3°C) measured at the location Krupa, and highest (12.5°C) at location Škrka II. The lowest July temperature is measured location Bjelave Čapljina (17°C) and the highest July temperature of 28.8°C measured at the location Svitava I. The temperature measurement during the July ranging ± 11.8°C. At least the water temperature changes in six measurements were recorded at the location of Ada Čapljina (± 6.8°C) and a maximum at location Svitava I where the water temperature was in the range ± 19.9°C.

The maximum value of electrical conductivity (CND) was measured in March 2016 at the location Škrka II (2680 µS cm^{-1}), and the lowest at the location Bivolje Polje in July of the same year (39 µS cm^{-1}). In the location Škrka II was observed and the largest oscillation value of CND which is in the range of 204 µS cm^{-1}, measured in January 2016. to 2680 µS cm^{-1} in March (± 1721.5 µS cm^{-1}) (Table 2).

Table 2. *Monitoring of electrical conducitivty.*

Location	Electrical conductivity (µS cm^{-1})					
	September 2015.	**January 2016.**	**March 2016.**	**May 2016.**	**June 2016.**	**July 2016.**
Ada Čapljina	342	318	325	336	319	339
Bjelave Čapljina	347	318	324	335	317	340
Trebižat	916	593	531	668	649	791
Čeljevo	406	422	325	337	383	441
Gabela	384	424	408	406	385	443
Svitava I	209	416	305	249	275	237
Svitava II	375	337	403	412	408	417
Višići-rukavac	906	464	401	403	401	399
Deransko lake I	425	405	433	453	434	438
Deransko lake II	400	408	425	450	436	431
Krupa	428	450	431	432	415	441
Karaotok	1394	1082	1889	1776	1743	1461
Škrka I	1624	1069	1202	1357	1042	1143
Škrka II	1600	204	2680*	2140	1900	1805
Klepci	623	317	338	340	381	362
Bregava	634	374	377	380	388	386
Počitelj	342	316	334	336	327	338
Ševaš Polje	347	316	333	337	326	338
Bivolje Polje	346	316	329	337	325	39*
Žitomislić	346	317	323	335	321	337

This research shows that the greatest salinity water lower flow of the Neretva River measured at the location Škrka II in March 2016 (1.5 PSU). Lower salinity of the river is in the range ± 1.5 PSU, round average is 0.23 PSU. The lowest salinity in the water at the average location Svitava I (AS = 0.033 PSU).

Table 3. *Monitoring of salinity.*

Location	Salinity (PSU)					
	September 2015.	**January 2016.**	**March 2016.**	**May 2016.**	**June 2016.**	**July 2016.**
Ada Čapljina	0,1	0,1	0,1	0,1	0,1	0,1
Bjelave Čapljina	0,1	0,1	0,1	0,1	0,1	0,1
Trebižat	0,4	0,2	0,2	0,2	0,2	0,3
Čeljevo	0,1	0,1	0,1	0,1	0,1	0,1
Gabela	0,1	0,1	0,2	0,2	0,1	0,1
Svitava I	0*	0,1	0*	0,1	0*	0*
Svitava II	0,1	0,1	0,1	0,1	0,1	0,1
Višići-rukavac	0,4	0*	0,1	0,1	0,1	0,1
Deransko lake I	0,1	0,1	0,1	0,1	0,1	0,1
Deransko lake II	0,1	0,1	0,1	0,1	0,1	0,1
Krupa	0,1	0,1	0,1	0,1	0,1	0,1
Karaotok	0,6	0,5	1	0,9	0,8	0,7
Škrka I	0,8	0,5	0,5	0,6	0,5	0,5
Škrka II	0,5	1	1,5*	1,1	1	0,9
Klepci	0,1	0,1	0,1	0,1	0,1	0,1
Bregava	0,2	0,1	0,1	0,1	0,1	0,1
Počitelj	0,1	0,1	0,1	0,1	0,1	0,1
Ševaš Polje	0,1	0,1	0,1	0,1	0,1	0,1
Bivolje Polje	0,1	0,1	0,1	0,1	0,1	0,1
Žitomislić	0,1	0,1	0,1	0,1	0,1	0,1

Total dissolved solids in water lower Neretva from a minimum of 203 mg L^{-1} as measured in January 2016 at the site Škrka II to 2680 mg L^{-1} in the same location in March 2016 and the measured values are in the range ± 2 477 mg L^{-1}.

Table 4. *Monitoring of total dissolved solids.*

Location	Total dissolved solids (mg L^{-1})					
	September 2015.	January 2016.	March 2016.	May 2016.	June 2016.	July 2016.
Ada Čapljina	343	318	324	336	319	339
Bjelave Čapljina	349	318	323	336	317	340
Trebižat	920	539	530	668	648	790
Čeljevo	409	423	323	336	382	340
Gabela	385	423	405	407	386	444
Svitava II	208	419	290	250	276	237
Svitava II	374	337	402	412	407	415
Višići-rukavac	902	465	403	403	402	400
Deransko lake I	425	406	433	453	439	436
Deransko lake II	401	408	425	450	436	431
Krupa	431	460	433	432	413	442
Karaotok	1396	1076	1910	1784	1746	1453
Škrka I	1620	1064	1202	1346	1045	1145
Škrka II	1610	203*	2680*	2150	1900	1806
Klepci	622	319	340	341	381	361
Bregava	634	373	376	380	387	386
Počitelj	341	315	333	336	326	338
Ševaš Polje	346	316	335	336	327	339
Bivolje Polje	346	316	330	337	325	340
Žitomislić	347	316	323	336	320	337

All values of dissolved oxygen at all locations were in the range of ± 8.6 mg L^{-1} (Table 5), and the average value of dissolved oxygen at all locations is 10.23 mg L^{-1}. The highest dissolved oxygen was measured in January 2016 at the location Klepci (12.6 mg L^{-1}), and the lowest in July at the location Karaotok (4 mg L^{-1} The water at the location Karaotok is the exception where determined average dissolved oxygen of 6.64 mg L^{-1} O_2 classifying them in second quality class according to Regulation on classification of waters B&H. Moderate best representation of dissolved oxygen in water are at locations Žitomislić (11.82 mg L^{-1}), Bivolje Polje (11.78 mg L^{-1}), Počitelj (11.69 mg L^{-1}) and Ševaš Polje (11.61 mg L^{-1}). While the lowest average representation is at locations Karaotok (6.64 mg L^{-1}) and Škrka II (8.63 mg L^{-1}).

Table 5. *Dissolved oxygen.*

Location	Dissolved O_2 (mg L^{-1})					
	September 2015.	January 2016.	March 2016.	May 2016.	June 2016.	July 2016.
Ada Čapljina	9,5	12,4	11,43	11,29	11,3	12,09
Bjelave Čapljina	9,38	12,58	11,47	11,24	11,26	12,06
Trebižat	10,66	11,41	11,25	10,28	10,48	10,02
Čeljevo	9,94	11,78	11,5	11,3	10,04	9,83
Gabela	9,68	11,88	11,06	11,37	9,98	9,99
Svitava II	9,77	10,19	11,35	10,7	8,78	10,96
Svitava II	6,52	11,5	10,76	8,89	9,61	4,7
Višići-rukavac	10,11	10,7	10,93	10,99	10,81	11
Deransko lake I	10,09	11,05	10,67	12,22	9,11	9,51
Deransko lake II	11,22	10,99	10,9	9,74	9	9,87
Krupa	8,86	10,6	10,85	8,6	5,42	7,48
Karaotok	4,06	10,4	7,83	7,8	5,75	4*
Škrka I	6,82	9,85	7,94	6,5	6,2	6,2
Škrka II	7	8,7	9,13	9,6	9	8,32
Klepci	9,47	12,6*	11,5	11,29	10	10,92
Bregava	9,37	11,36	10,96	10,59	10,36	9,7
Počitelj	12,3	12,18	11,4	11,32	11,05	11,88
Ševaš Polje	12,05	12	11,3	11,4	11	11,9
Bivolje Polje	12,28	12,48	11,59	11,41	11,02	11,92
Žitomislić	12,22	12,33	11,63	11,38	11,52	11,84

Saturation below 80% indicates an increased oxygen consumption, which is established as locations Karaotok (63.23% O_2) and Škrka I (72.7% O_2).

The range of the measured pH of the studied area is from 7.2 measured at location Škrka I on May 2016. To 8.5 at the location Počitelj in September 2015. (± 1.3).

The highest variation in the measured pH values are recorded during the measurement in September 2016 and July 2016 (± 1.1). Observed by the locations, the highest variation of pH was observed at the site of Svitava II (± 1.1), and at least oscillated pH value at Gabela (± 0.1) (Table 6).

Table 6. *pH.*

Location	pH					
	September 2015.	**January 2016.**	**March 2016.**	**May 2016.**	**June 2016.**	**July 2016.**
Ada Čapljina	8,1	8,2	8,1	7,9	8	8,3
Bjelave Čapljina	8,2	8,2	8,1	8	8,1	8,4
Trebižat	8,1	8,2	8,1	7,9	8,1	8,2
Čeljevo	8,1	8,2	8	8	8,1	8,1
Gabela	8,2	8,2	8,1	8,1	8,2	8,2
Svitava I	8,3	8,1	8,3	8,1	7,8	8,2
Svitava II	7,9	8,4	7,9	7,7	7,6	7,3
Višići-rukavac	7,8	8	8	8	8	8,1
Deransko lake I	8	8,1	8	7,9	8,2	7,9
Deransko lake II	8,2	8,1	8	8	8,2	7,9
Krupa	7,9	8,03	7,9	7,8	7,7	8
Karaotok	7,4	8,3	7,7	7,7	7,5	7,65
Škrka I	7,7	7,8	7,5	7,2*	7,5	7,5
Škrka II	7,8	7,5	7,6	7,5	7,7	7,8
Klepci	7,5	8,1	8	7,9	8	8,1
Bregava	7,5	8,3	8,1	8	8,1	8
Počitelj	8,5*	8,2	8,1	8	8,2	8,3
Ševaš Polje	8,4	8,1	8	8	8,1	8,3
Bivolje Polje	8,45	8,2	8,1	7,9	8	8,3
Žitomislić	8,5	8,2	8	8	8	8,2

According all locations and all measurements the variability of the temperature is moderate (V = 30%). The average water temperature of the study area was 14.3°C, the standard deviation is σ = 4.5°C.

The average electrical conductivity of the water study area is 560.8 μScm^{-1} (σ = 458.52 μScm^{-1} and at 82% of the variability that is very strong (V ≥ 70%).

Statistically established that the average deviation from the average salinity σ = 0.26 PSU and the variability of salinity very strong (V = 115%). The salinity of the study has a mean value of 0.23 PSU.

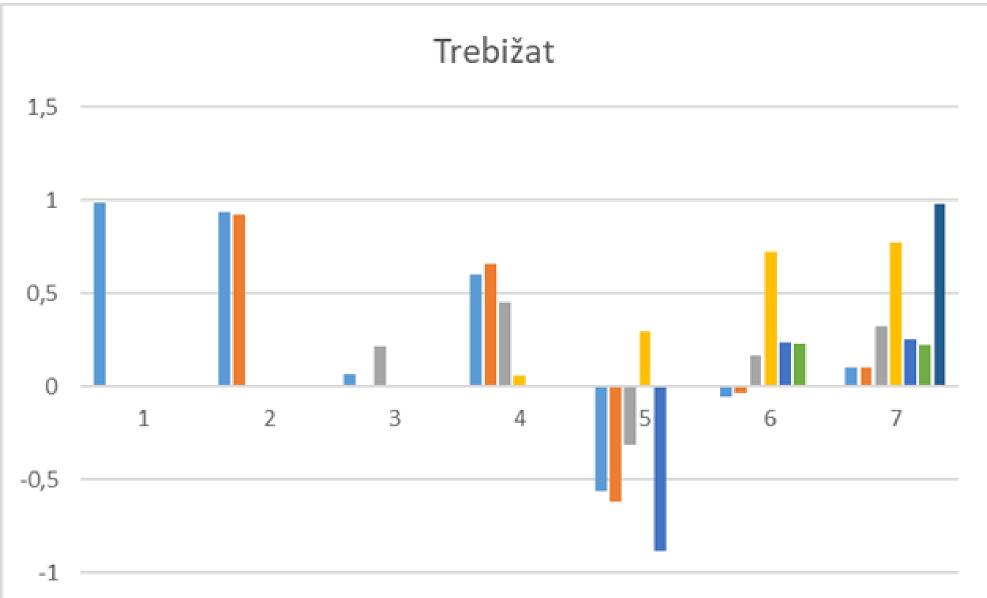
The average value of total dissolved solids is 562.27 mg L^{-1} (σ =457.68 mg L^{-1} with a very strong variability, V = 81%).

In the investigated area the average value of dissolved oxygen of 10.23 mg L^{-1} (σ = 1.84 mg L^{-1}). Variability of dissolved oxygen was 18%, and relatively weak (V = 10-30%).

The average percentage of dissolved oxygen in the investigated locations is 98.96% (σ = 16.60%). The variability of the percentage of dissolved oxygen is relatively low at 18%.

pH of the eighth among the measured values is determined from the average deviation σ = 0.25 or the pH variation is very weak, V = 3%.

Pearson correlation of location with increased salinity is shown on figure 1.



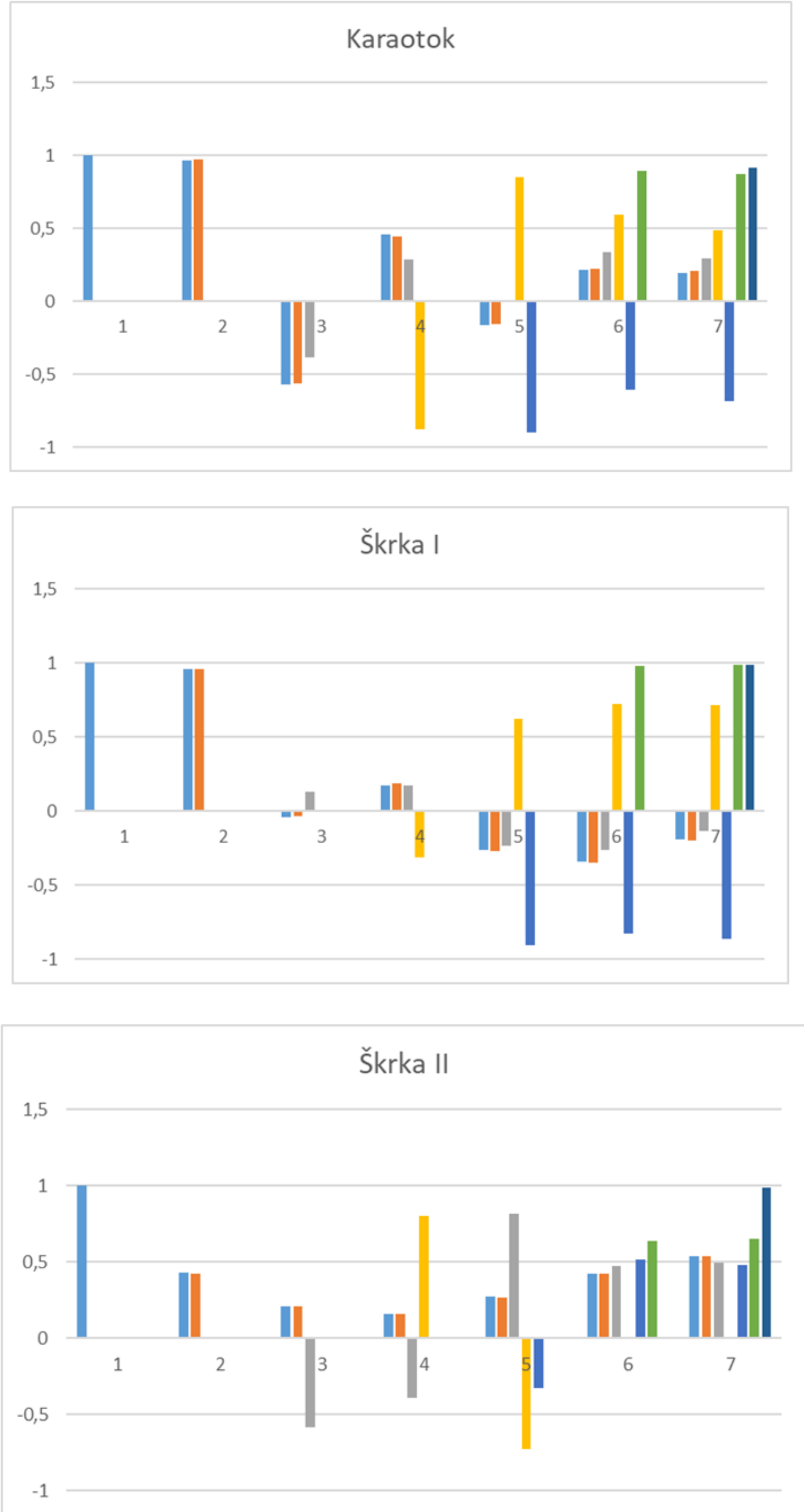


Figure 1. *Graphic review of Pearson correlation of measured water parameters at increased salinity locations.*

4. Discussion

Climate factors affect to the value of temperature measured during monitoring in the lower course of the river Neretva which have no uniform trend and occur significant fluctuations in the measured values.

Minimum temperature at all locations measured in January, expected and the highest in July 2016, which confirms the great influence on the water temperature has an air temperature.

Water temperature in the river flow are not constant and its changes under the influence of air temperature (climate), temperature of water which is supplied, the depth, length and speed of the water flow.

The measured value of electrical conductivity can assess the degree of mineralization of water and also to evaluate of the kind of water [9]. Accordingly, the water at locations Karaotok, Škrka I and II Škrka with an electrical conductivity measured value of more than 1000 $\mu S\ cm^{-1}$ are to be classified in brackish water [10].

The waters of the lower course of the Neretva river are exposed to salinization, and the main cause of salinization represents proximity to the sea. Neretva riverbed at the mouth of the very deep, 9 to 11 meters and can be treated as a small bay. This is very suitable for the penetration of seawater upstream, especially for the low water level when the Neretva flow lower energy. In the summer months, especially during high tide, strengthens the size and penetration of the salt wedge, which is denser and heavier and underlines under a layer of fresh river water and flow upstream [11].

Salinity increases with increasing temperature in summer and spring when the reduced upstream water flows.

It is important to point out in the context of increased salinity that altitude of locations with increased salinity is not the lowest on researched area. This implies that groundwater flows may also affect increased salinity. This statement is offered as one of the possible options, but additional studies should certainly be carried out for its confirmation.

Expected, the same locations have also increased electrical conductivity and total dissolved solids but lower dissolved oxygen. Only location Trebižat does not have decreased amount of dissolved oxygen, which can be caused by faster stream flow of the river.

According to the Regulation on classification of waters B&H [12] values of dissolved oxygen are high quality water (I class). Values of dissolved oxygen and salinity are confirming that the larger the salinity reduces the solubility of oxygen in water [13].

Oxygen saturation is a relative measure that indicates the percentage of oxygen dissolved in water in the normal solubility at a given temperature. Critical conditions often occur in summer in stagnant waters due to the cumulative effect of high temperature (less O_2), enhanced degradation of organic matter (spent O_2) and more rapid metabolism of the whole community [13].

According pH all ground water can be divided into two basic types: water with a neutral-alkaline reaction (pH rarely less than 6, and in many cases is increased up to 10) and water with an acidic (pH <5). The measured pH values are fairly uniform, and their average value is pH 8 as the lower water of the river puts in goods alkanes water suggesting oligotrophic status of these waters [14].

There is a weak positive correlation ($r = 0.17$) between the temperature (T) and electrical conductivity (CND) water and the temperature climbs and electrical conductivity of the water in line with expectations [14].

There is weak negative correlation ($r = - 0.48$) between the temperature (T) and the total dissolved oxygen (O_2) or by reducing the temperature of water increases the water saturation of dissolved oxygen in accordance with previous studies [15].

Moderate negative correlation ($r = - 0.51$) was found between the total dissolved oxygen (O_2) and salinity which means that the total oxygen content slightly decreases with increasing salinity [16].

Functional positive relationship ($r = 1$) exists between the total dissolved solids (TDS) and electrical conductivity (CND) water or an increase in total dissolved solids also increases the electrical conductivity of which is expected, since the electrical conductivity is an indirect measure of the total dissolved solids [9].

According four locations with increased salinity there is a complete correlation ($r = 0{,}92$-$0{,}97$) between salinity and conductivity, and total dissolved solids also at locations Trebižat, Karaotok and Škrka I. Since location Škrka II does not show strong but medium strong positive. This is most likely to be due to the fact that salinity is highest and most variable at the location of the Škrka II. According also week negative ($r = -0{,}33$) and medium positive correlation ($r =0{,}51$) between temperature and dissolved oxygen and oxygen saturation at the same location it is recommendable to investigate eventual eutrophication.

5. Conclusions

Water of the lower river Neretva are within the limit values for the water I and II class of quality according to the Regulation on classification of waters B&H.

Maritime impact from downstream side and built hydroelectric system with the upstream side make water regime in the lower course of the Neretva River is very complex.

Everything that happens in the lower course of the river Neretva is the result of what happens upstream, and the impact of salt water from Metković to downstream.

During the summer period, flows into the Neretva are very small, and then the impact of the tides and the greatest.

The average deviation from the average salinity $\sigma = 0.26$ PSU. The total oxygen content slightly decreases with increasing salinity. Salinity is highest and most variable at the location of the Škrka II.

It is recommended to continue research on four locations with increased salinity, Trebižat, Karaotok, Škrka I and Škrka II, in hydrological and biological aspects especially eutrophication.

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