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Research Paper

The Microbiological and Physico Chemical Quality of Surface and Groundwater's of Buna River-Protected Landscape and Velipoja (Albania)

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Abstract. The hydrographic complex system of Lake Shkoder-River Buna, Velipoja Coast-Viluni lagoon covers a very important wetland area in regional level (South-Eastern Adriatic Sea) and is a key of importance to the natural and socio-economic processes. River Buna is the unique outflow in the south-eastern part of Shkoder Lake, and discharges its waters in Buna delta in Velipoja, 44 km far from Shkoder. The main activities in the region are agriculture, fishing, stock raising and tourism. Main threats of surface and groundwater's in this area are anthropogenic pollution, effluent generated by livestock, precipitations etc. This paper aims providing some evaluations to water quality in terms of physical-chemical and microbial pollution of the surface and ground water in that region. In the frame of water quality assessment in Buna river-Velipoja protected landscape, were organized six sampling campaigns respectively on April-July 2019. The assessment of water quality in the Buna Delta Velipoja-Protected Landscape was done by analyzing of thirteen physical-chemical parameters and microbiological analyses *(E. coli)* in seven sampling stations of surface water and four sampling stations for underground water. The quality of surface water is indicated from wastewater direct discharges of Shkoder city in river Buna and ground water quality mainly form agriculture. The parameters that were higher than EU standards were *E. coli* during summer time for both surface and groundwaters and Cl^-, conductivity because of intrusion of saline water into freshwater aquifers. Surface and underground waters of Buna river-Velipoja protected landscape plays an important ecological role in ecosystem preservation. Underground waters are widely used by the resident population for agricultural purposes and drinking. This region is risked by anthropogenic activities, which affect the quality of natural water ecosystems.

Keywords: *anthropogenic, livestock, turbidity, temperature, conductivity, E. coli.*

Introduction

The Buna River (44 km long) is the second tributary after Po in the Adriatic Sea; it drains from Lake Shkodra, the largest Balkan lake and receives Drin flow, the longest Albanian river (Tockner, 2009). Buna Delta has a surface area of approximately 90.7 km^2, and according to the classification, in terms of its processes (Landscape Albania, 2015), it is fluvial dominated, clay dominated (clay and silt) and ribbed. Within the framework of the National Biodiversity Strategy, in 2005, the Albanian government established the Buna River-Protected Landscape (BRPL), which includes the Buna River area with the delta area and the Viluni lagoon. The Buna River is also included in the European Green Belt, but this status must be reconceived as a biosphere reserve (Rakaj, 2012). The serious problems in the coastal waters are inflicted due to the anthropogenic influence. The unsolved problem of wastewater disposal leads to the pollution of toxic bacteria and eutrophication (Regner, 2002). Most of the communes in the area have no sewage system or wastewater treatment plant, with the exception of some major villages representing approximately from 5 to 10 % of the total population living in the area; even in those cases, the wastewater collected is discharged directly into the rivers or sea (Barbieri, 2015). Albanian development has been characterized by a lack of formal planning and informal development. The recent boom in construction boom, dating from the 1990s, has

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affected in particular the coastal region and urban centres. (IRMP Buna-Bojana area). The assessment of water quality in the Buna Delta-Velipoja Protected Landscape the sampling, physico-chemical and microbiological analyses were conducted in seven sampling points of surface waters and four sampling stations for underground waters. The aim of this study was the evaluation of water quality of Buna Delta-Velipoja Protected landscape by measuring different parameters as: temperature, dissolved oxygen, electrical conductivity, turbidity, PO_4^{3-}, NO_3^-, *Escherichia coli etc.* The presence of *Escherichia coli, Intestinal enterococci* and the other coliform bacteria in surface water depends on input wastewaters, septic drainage, agricultural sources, animal waste, during rainfalls, etc. *Escherichia coli* is an indicator of faecal pollution and water contamination (Todar, 2007).

Materials and Method

Study Area

The hydrographic complex system of Lake Shkoder -River Buna, Velipoja Coast-Viluni lagoon covers a very important wetland area in regional level (South-Eastern Adriatic Sea). Geographic coordinates of sampling stations are given in maps 1 and 2 (Figure 1a & 1b). The assessment of water quality in the Buna Delta-Velipoja Protected Landscape the sampling, physico-chemical and microbiological analyses were conducted in seven sampling points of surface water and four sampling stations for underground waters given with geographical coordinates in the Table 1.

Table 1. Geographical Coordinates of Sampling Stations

Nr	Sampling stations	Geographic coordinates
1	Zues	42°01'37.4"N; 19°28'19.9"E
2	Pulaj1	41°54'53.7"N; 19°21'14.7"E
3	Pulaj 2	41°52'50.2"N; 19°22'45.0"E
4	Buna Estuary	41°51'56.8"N; 19°22'33.3"E
5	Lagoon of Vilun	41°52'04.0"N; 19°27'12.1"E
6	Vilun sea	41°51'27.8"N; 19°26'10.6"E
7	Velipoje sea	41°51'38.3"N; 19°25'35.7"E
8	Obot	41°59'24.7"N; 19°25'42.7"E
9	Dajc	41°59'39.7"N; 19°24'46.5"E
10	Pentar	41°57'31.7"N; 19°22'27.8"E
11	Velipoje (Well)	41°51'59.0"N; 19°25'36.9"E

Figure 1.a Map of four sampling stations for underground waters

Figure 1.b Map of seven sampling stations for surface waters

Experimental Study

The period of sampling waters samples from Buna river complex system of Lake Shkoder-River Buna, Velipoja Coast-Viluni lagoon and underground waters was done during the period April-July 2019. The samples collected were analyzed for physical-chemical and microbiological parameters. The technical sampling and analyses procedures were done in accordance with TESSA methodology (two parallel samples were taken for each station). The water samples for underground waters were taken in four sampling point in figure 1.a and samples for surface water were taken in seven sampling point in figure 1.b. The samples were analyzed for eight physical-chemical parameters for seven samples of surface waters and eleven physical-chemical parameters for four samples of underground waters and only one microbiological parameter *Escherichia coli* was analyzed for surface and underground waters. The analytical methods used for each physical-chemical and microbiological parameter are included in the tables 2 and 3. Microbiological quality for waters samples for surface and drinking waters were determined by the standard method most probable number (MPN). Most Probable Coliform Number (MPN) method for *Escherichia coli*, was carried out in the water samples after the necessary dilution; 10 mL of the sample was inoculated into three tubes each with double strengths tubes, one millilitre was inoculated into each of first three single strength tubes, and 0.1 mL sample was inoculated into each one of the other three tubes, all containing lactose broth medium. The tubes were incubated at 44°C for 24-48h, during this period, the gas accumulation in Durham tubes was observed and The Most Probable Coliform Number was determined using the MPN index (Finstein, 1972). The faecal coliforms group includes all of the rod-shaped bacteria that are non-spore forming, *Gram-Negative*, lactose-fermenting in 24-48 hours at 44.5°C, which can grow with or without oxygen. Gas production within 24 hours is considered a positive reaction indicating coliforms of faecal origin. The results are reported as most probable number (MPN) of faecal coliforms/100 ml (APHA/AWWA/WPCF (1998). (International Standard ISO 9308-2 (1990) was used for detecting and enumerating coliform organisms, thermotolerant coliform organism and presumptive *Escherichia coli*. First edition**.** Part 2: Multiple tube (most probable number) method. First edition 1990-10-01**.** ISO 9308-2 (1990). MPN/*Escherichia coli* results for Buna river Velipoje protected landscape (surface waters).

Table 2. Analytical methods of physical-chemical and microbiological analyses of surface water

Nr	**Parameter**	**Method of analysis**
1	*pH	S SH EN ISO 10523:2012
2	Temperature	Thermometry
3	*Conductivity	S SH EN 27888:2001
4	*Turbidity	S SH EN ISO 7027:2001
5	*NO_3^-	S SH ISO 7890-3:2000
6	DO	S SH ISO 17289:2014
7	PO_4^{3-}	APHA/AWWA 424 F/1995
8	BOD	S SH ISO 5815-2:2009
9	*Escherichia coli/MPN*	ISO 9308-2/1990

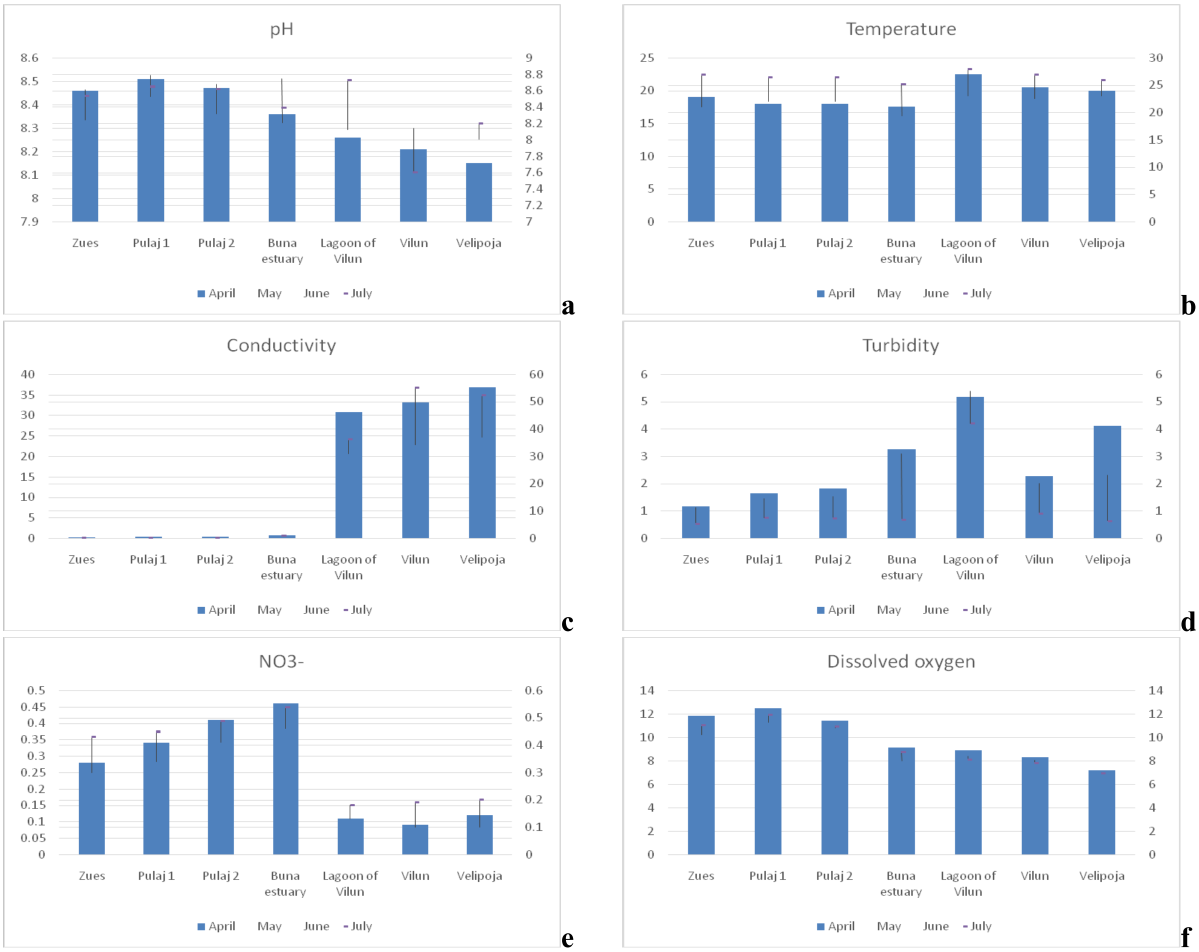
Table 3. Analytical methods of physical-chemical and microbiological analyses of groundwater

Nr	**Parameter**	**Method of analysis**
1	pH	S SH EN ISO 10523:2012
2	Temperature	Thermometry
3	Turbidity	S SH EN ISO 7027:2001
4	*Conductivity	S SH EN 27888:2001
5	TDS	Indirect method from Conductivity
6	*NO_3^-	S SH ISO 7890-3:2000
7	PO_4^{3-}	APHA/AWWA 424 F/1995
8	*Cl^-	S SH ISO 9297:2000
9	$SO4^{2-}$	APHA/AWWA 426 C/1995
10	DO	S SH ISO 17289:2014
11	BOD	S SH ISO 17289:2014
12	*Escherichia coli/MPN*	ISO 9308-2/1990

Results and Discussion

Surface Water

The pH ranged between 7.6 and 8.79 Figure 2 (a) with and all the sampled waters showed pH values close to neutral or slightly alkaline. Temperature values ranged from 17.5 to 28.0 °C, Figure 2 (b) during the four months of survey. Electrical conductivity (EC) values ranged from 0.198 - 55.1 mS/m, Figure 2 (c). The turbidity ranged 0.65-5.4 NTU, Figure 2 (d), and meets the EU limits. The other results of physical chemical analyses of surface waters from Buna River and Velipoja coast showed low concentration of the NO_3^- figure 2 (e) and PO_4^{3-} figure 2 (g) and there are no values that exceed the thresholds recommended by European Standard. The NO_3^- concentration ranged 0.9-0.54 mg/L, Fig 2 (e) and PO_4^{3-}concentration ranged 0.01- 0.03 mg/L Fig 2(g) during all periods of monitoring. The nutrient NO_3^- was higher during the June and July Fig 2 (e) because of the higher temperatures of water and intensification of the eutrophication process. The DO ranged 6.9-12.5 mg/L, Fig 2 (f) and BOD 2.5- 4.25, Fig 2 (h) values showed that they did not exceed the EU Limits. These results show that the water quality of river Buna and Velipoja coast meets the EU limits. Based on Directive 2006/7/EC for inland waters, coastal and transitional waters our sampling points Lagoon of Vilun, Vilun, Velipojë, Zues, Buna estuary, River Pulaj 1 met the Directive for *Escherichia coli* for Excellent quality/250 CFU/100mL water, Class (A), Figure 2 (k). The microbiological parameter of *Escherichia coli/MPN* was higher only on the point Pulaj 2 Figure 2 (k) for surface waters with 260 CFU/100 mL water, which classify them as good quality (B) 500 CFU/100 mL water according the Directive 2006/7/EC for inland waters, coastal and transitional waters.



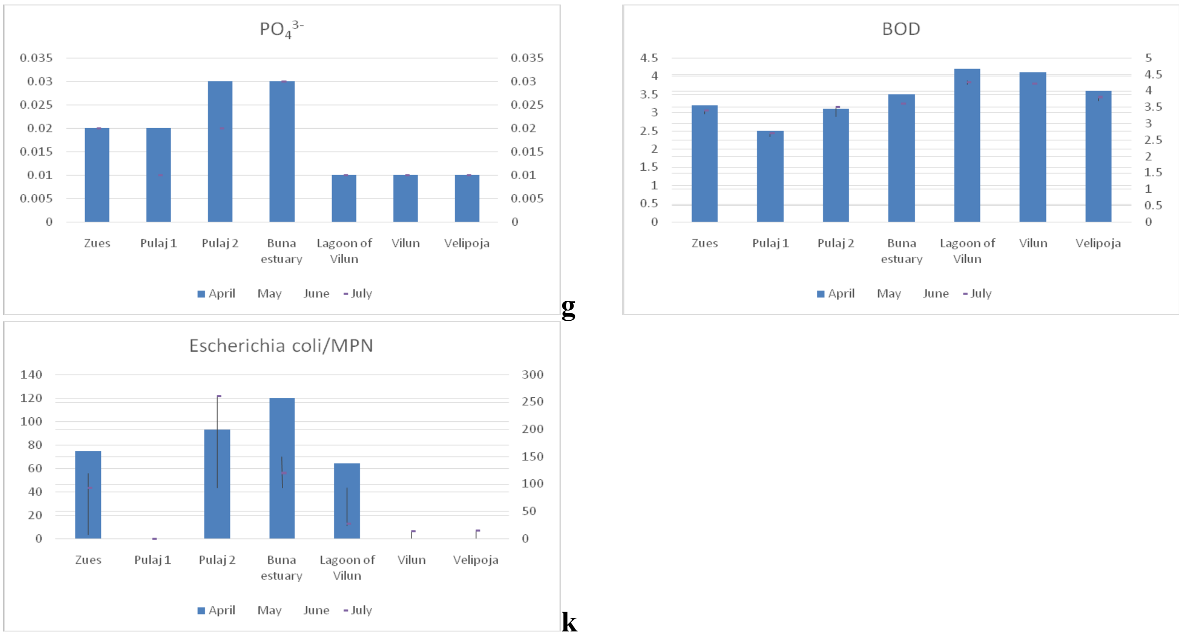


Figure 2. (a,b,c,d,e,f,g, h, k). Histograms in Excel for physico-chemicals and microbiological parameters (a-pH, b-temp, c-conductivity, d-turbidity, e-$NO3^-$, f-dissolved oxygen, g- PO_4^{3-}, h-BOD, k-*Escherichia coli*/MPN)

Statistical processing was conducted by Minitab 17, Statistical program. In the Figure 3 (a, b, c, d) the results of our study are presented with probability plot graphics for different months April, May, June, July 2019 for surface waters in different sampling points Lagoon of Vilun, Vilun, Velipojë, Zues, Buna estuary, River Pulaj 1, Pulaj 2. The P-Value for every parameter was less than 0.05 (*P*<0.05), which indicates strong evidence against the null hypothesis. A null hypothesis is a type of hypothesis used in statistics that proposes that there is no difference between certain characteristics of a population or data-generating process).

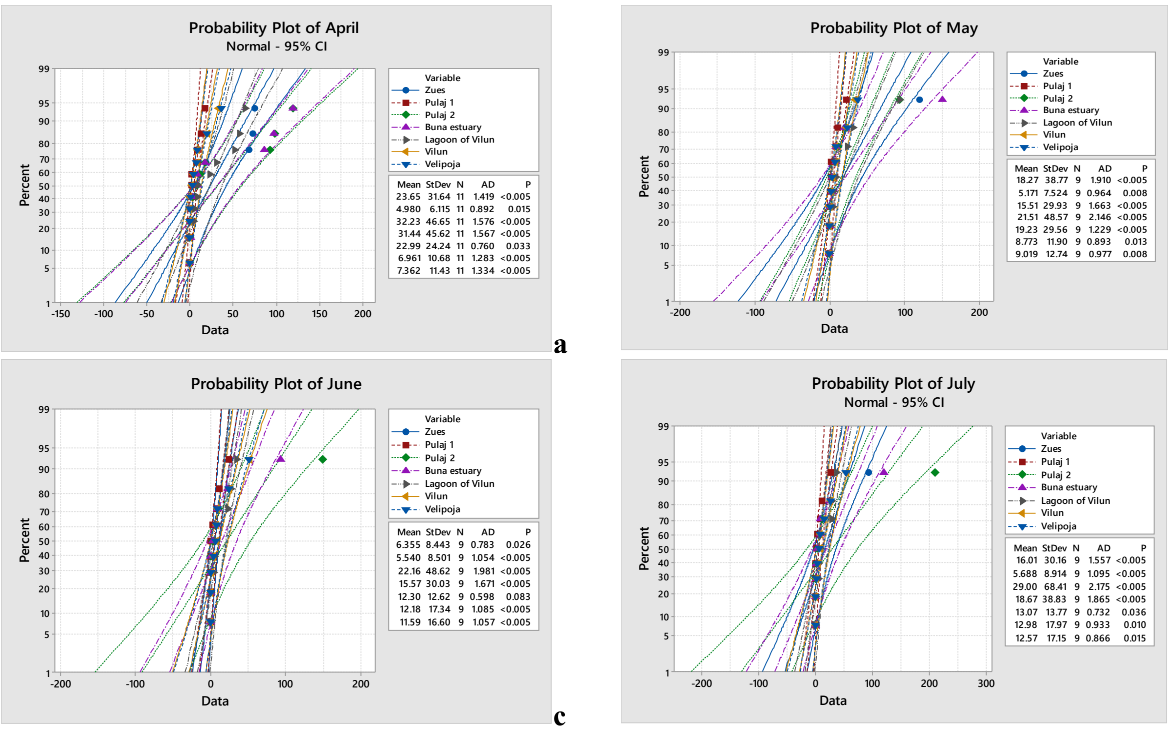


Figure 3. (a,b,c,d). Probability plot for different months (a-April, b-May, c-June, d-July).

Underground Water Results

Temperature values ranged from 15 to 20°C during the monitoring period for months April-July, table 4, 5, 6 and 7. The pH ranged between 8.11 to 8.5 and all the sampled waters showed pH values close to neutral or slightly alkaline, table 4, 5, 6 and 7. Electrical conductivity (EC) values ranged from 0.313-41.84 mS/m, table 4, 5, 6 and 7. The station that has the higher Electrical conductivity values was Pentar. TDS values ranged from 256 to 1260. mg/l, table 4, 5, 6 and 7. The turbidity ranged 0.03-0.89 NTU and meets the EU limits for drinking water. The physical-chemical analyses of underground water showed low concentration of the NO_3^- and PO_4^{3-} and there are no values that exceed the thresholds recommended by European Standard. The NO_3^- concentration ranged 0.05-4.2 mg/L and PO_4^{3-} concentration ranged 0.07-0.34 mg/L during all periods of monitoring, table 4, 5, 6 and 7. The DO ranged 5.4-7.1 mg/L and BOD 0.8-1.5, values showed that they did not exceed the EU Limits. The Cl^- concentration ranged from 19.8-170 mg/L, which do not exceed the EU limits, table 4, 5, 6 and 7. The increasing of chloride concentrations in Velipoja and Pentar wells may be the first indication of the approach of a seawater contamination front. In an area where no other source of saline contamination exists, high chlorine concentrations in groundwater can be considered rather definitive proof of seawater contamination. Other underground water samples have low Cl^- concentrations. The SO_4^{2-} ranged from 9-50.1 mg/L and meets the EU Standard. These results show that the underground water meets the EU limits. The most contaminated well was in Pentar sampling point, this well in Pentar does not meet the EU norms because of high values of TDS. This well in Pentar is used from different inhabitants as drinking water. There were some villages in the Buna River-Protected Landscape that do not have a drinking water supplying system and use their own wells as drinking water or supply with drinking water in other villages. Groundwater is generally considered a “safe source” of drinking water because it is abstracted with low microbial load with little need for treatment before drinking. Amount of groundwater’s for potable and industrial waters use is varying from 70 to 93% of total water consumption (Cemsa, 2012). *The main requirement concerning the quality of water for public use* is that they must be "healthy" to use. Requirements of standards for drinking water quality are very strict. European Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, does not allow the content of any colony of *E.coli* in 100 ml of water. Based on the Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption the samples for drinking waters results at good quality in Obot, Pentar, Velipoje where *Escherichia coli* with the MPN method was not detected with one exception in the sample Dajç, which resulted with a low loading with *Escherichia coli* for 3CFU/100 mL.

Table 4. Underground water results for month April

Parameter	Velipoja	Obot	Pentar	Dajç	EU/WHO Norms for drinking water
***pH**	8.12	8.33	8.11	8.32	6.5-8.5
Temperature	17	15	17	17	-
***Odor**	Negative	Negative	Negative	Negative	Odourless
***Taste**	Normal	Normal	Normal	Normal	Tasteless
***Turbidity**	0.03	0.06	0.84	0.22	4
***Conductivity**	550	373	1810	397	1400
TDS	369	249	1212	265	1000
***NO_3^-**	3.89	0.08	0.05	0.07	50
PO_4^{3-}	0.07	0.09	0.15	0.36	-
***Cl^-**	50.1	25.5	164	19.8	250
$SO4^{2-}$	15	12	45	10	250
DO	5.9	6.8	6.2	6.6	>5
BOD	1.2	0.9	1.4	1.1	5
E. coli/MPN	0	0	3	2	0

Table 5. Underground water results for month May

Parameter	Velipoja	Obot	Pentar	Dajç	EU/WHO Norms for drinking water
***pH**	8.34	8.14	8.21	8.45	6.5-8.5
Temperature	18	17	19	18	-
***Odor**	Negative	Negative	Negative	Negative	Odourless
***Taste**	Normal	Normal	Normal	Normal	Tasteless
***Turbidity**	0.06	0.04	0.79	0.17	4
***Conductivity**	547	383	1834	401	1400
TDS	366	256	1228	268	1000
***NO_3^-**	4.1	0.1	0.07	0.1	50
PO_4^{3-}	0.08	0.11	0.18	0.32	-
***Cl^-**	52	27	170	20.4	250
$SO4^{2-}$	17	15	47	9	250
DO	5.6	7.1	6.02	6.5	>5
BOD	1.3	0.8	1.5	1.1	5
E. coli/MPN	0	0	0	3	0

Table 6. Underground water results for month June

Parameter	Velipoja	Obot	Pentar	Dajç	EU/WHO Norms for drinking water
***pH**	8.25	8.24	8.16	8.5	6.5-8.5
Temperature	19	18	19	19	-
***Odor**	Negative	Negative	Negative	Negative	Odourless
***Taste**	Normal	Normal	Normal	Normal	Tasteless
***Turbidity**	0.02	0.06	0.83	0.21	4
***Conductivity**	562	394	1860	434	1400
TDS	376	263	1246	290	1000
***NO_3^-**	3.67	0.07	0.11	0.09	50
PO_4^{3-}	0.12	0.11	0.16	0.34	-
***Cl^-**	54	25	173	22	250
$SO4^{2-}$	16	18	50.1	10.3	250
DO	5.4	6.7	6	6.3	>5
BOD	1.4	0.9	1.5	1.2	5
E. coli/MPN	0	0	0	0	0

Table 7. Underground water results for month July

Parameter	Velipoja	Obot	Pentar	Dajç	EU/WHO Norms for drinking water
***pH**	8.18	8.35	8.16	8.34	6.5-8.5
Temperature	19	18	20	19	-
***Odor**	Negative	Negative	Negative	Negative	Odourless
***Taste**	Normal	Normal	Normal	Normal	Tasteless
***Turbidity**	0.03	0.08	0.89	0.27	4
***Conductivity**	560	387	1847	423	1400
TDS	375	259	1237	283	1000
***NO_3^-**	3.79	0.08	0.12	0.1	50
PO_4^{3-}	0.12	0.13	0.16	0.32	-
***Cl^-**	56	26.4	168	20.7	250
$SO4^{2-}$	20	16	48	11	250
DO	5.7	6.7	6.1	6.3	>5
BOD	1.4	0.9	1.5	1.2	5
E. coli/MPN	0	0	0	0	0

Statistical processing was conducted by Minitab 17. Statistical program was used also for underground waters. In the figure 4 (a, b, c, d) the results of our study were presented with probability plot graphics for different months April, May, June, July 2019 for underground waters in different sampling points Velipoja, Obot, Pentar, Dajç. The P-value was ($P<0.05$) for all parameters. If the p-value is 0.05 or lower, the results are significant.

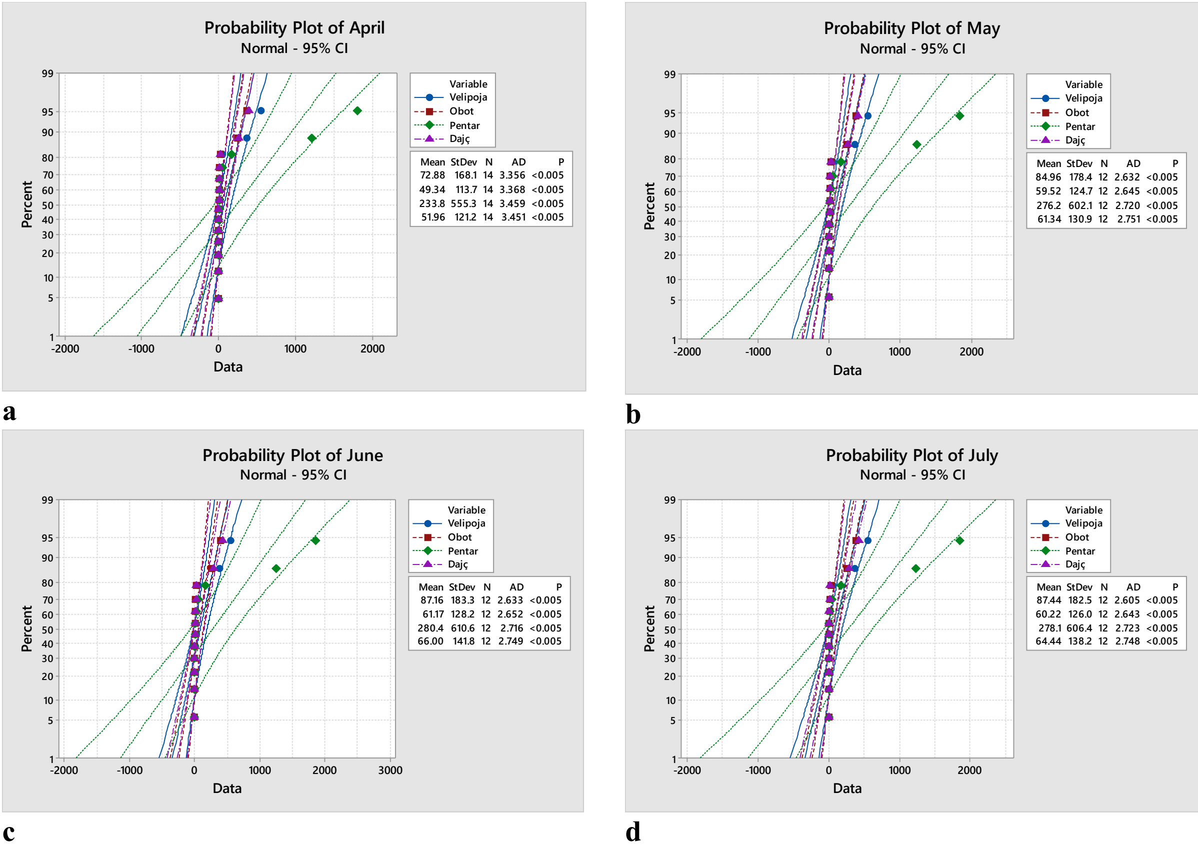


Figure 4. (a,b,c,d). Probability plot for different months (a-April, b-May, c-June, d-July for underground waters).

Conclusions

Surface and underground of Buna river Velipoja protected landscape plays an important ecological role in ecosystem preservation. Underground water is also widely used by the resident population for agricultural purposes and drinking. The physical-chemical and microbiological parameters of surface water and underground water meet the EU norms except Pentar underground water. The wastewater treatment plant of Velipoja has influenced in the improving of the microbiological water quality in Velipoja coast. The construction of other wastewater treatment plants in Buna River-Protected Landscape villages and drinking water supply will protect the river Buna and Velipoja coast water from anthropogenic pollution and will increase the quality of life of the community by the use of safe drinking water.

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