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STATE OF WATER QUALITY FOR REBRICEA RIVER BY PRINCIPAL COMPONENT ANALYSIS

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ABSTRACT

Water quality is one of the nowadays matters that benefits of numerous studies, as result of human society acknowledging the impact on the Hydrosphere. On this subject were identified inadequacies between the existing water resources and the upward trend in consumption demand of residents. This study represents an intermediate stage in the seasonal analysis of water quality parameters for the middle sector of Rebricea river in the administrative area of commune Scanteia (Iași county). Scanteia administrative territory is composed of seven villages: Bodesti, Borosesti, Ciocarlesti, Lunca Rates, Rediu, Scanteia and Tufestii de Sus and has 4781 residents. The most important villages cross in the 27 km length of the river are Carbunari, Grajduri, Scanteia, Rebricea. In the analyzed sector the land-use is predominantly agricultural, the activities have rural specifics. The aim of the study is to quantify the water quality based on statistical method and to identify variables that influence the water quality. Were collected samples from 20 points across the river for two seasons. The analyzed parameters are pH, NO_3^-, NO_2^-, GH (General Hardness), KH (Total Alkalinity) and temperature. Preliminary results range between 5.5-8.5 for pH, 0-40 ppm for NO_3^-, 4-56 °dH for GH, 6-16.8 °dH for KH and 0 ppm for NO_2^-. The specifics of the rural settlements and the land use imprint the characteristics of streams, also the absence of a water supply network has a major role in establishing chemical changes. As a result, have been distinguished relationships between impacts on water resources, land-use and demographic characteristics of the landscape.

Keywords: seasonal variation, water resources, rural hydrology

1 INTRODUCTION

Water quality is an important element in Hydrology as a component of a society that is concerned for the well-being of this greatest system–Earth. As part of European Union, Romania has integrated policies that promote a sustainable environmental framework. On these terms there are transposed in National legislation laws concerning water resources. The studies in this field are emphasizing the water stress issues that are caused by pressures on quality and the quantity of water resources (Breaban and Oiste, 2012, Gorde and Jadhav, 2013, Romanescu et al. 2014, 2015, 2016). In this case it is essential to evaluate the ecological status of surface water bodies. European Community Water Framework Directive records 5 states of quality, namely: high, good, moderate, poor and bad with the corresponding color code - blue, green, yellow, orange and red.

Rebricea river is located in North-Eastern Romania, the river basin being a component of Moldavian Plateau. The general landscape of cuesta forms is characterized by an elongated shape and a North-South orientation, in this case is easy to notice the altitude decreasing following this direction (Bacauanu et al., 1980). In the Rebricea basin the geologic cover is composed of Neogene–Sarmatian (Basarabian and Chersonian), Pleistocene and Holocene deposits. Water resources characteristics are strongly influenced by this geological substrate.

The monitoring seasonal analysis of water quality parameters for middle sector of Rebricea river in the administrative area of commune Scanteia (Iași county) has begun along with this first two seasons of the present study. This intermediate stage is important to identify the characteristics of surroundings and how they affect the quality of surface water. The section selected is overlaying administrative territory of Scanteia (Fig.1). For this study, the presence of seven distinct villages (Bodesti, Borosesti, Ciocarlesti, Lunca Rates, Rediu, Scanteia and Tufestii de Sus), a population of 4781 residents (Scanteia Village Hall, 2014) absence of a water supply network and the specifics of land use are few of the reasons behind selecting the area.

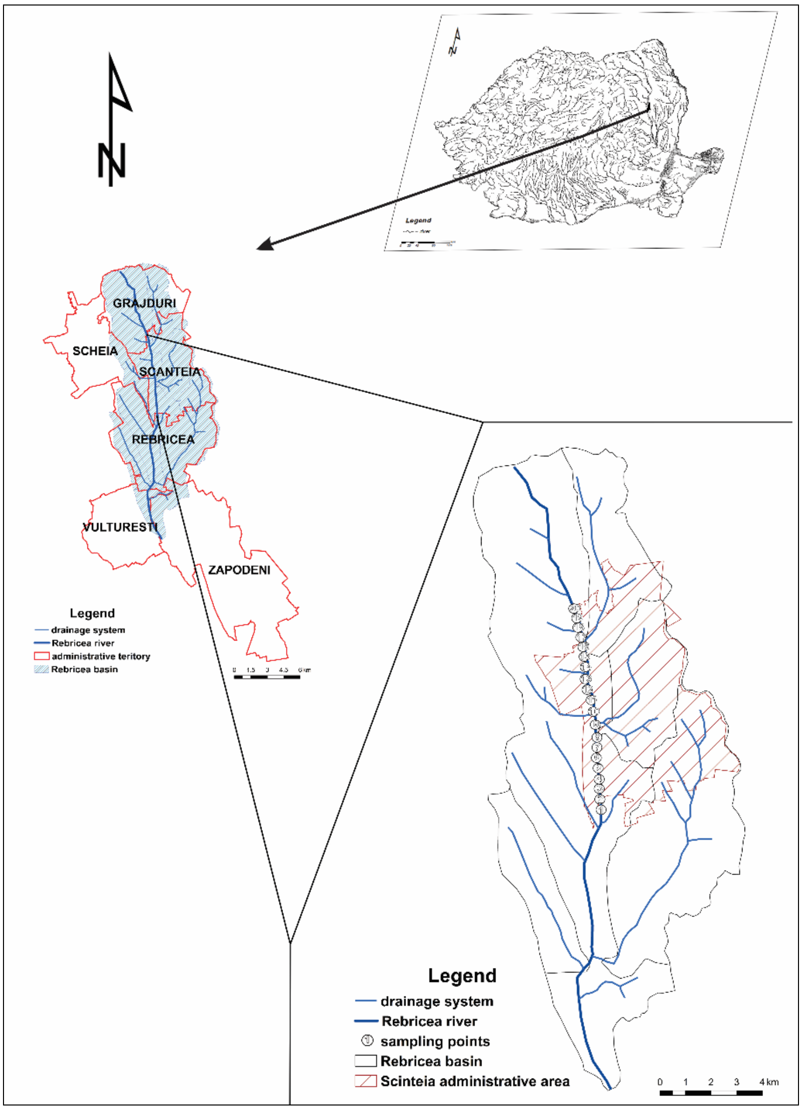

Figure 1. Rebricea river basin and sampling points localization

2 METHODOLOGY

The maps were generated by using the SRTM in Stereo 70 and created a mask consisting of the basin limit for the raster extraction process in ArcGIS 10.2. Corel DRAW X5, Microsoft Excel and XLSTAT 2016 were also used in making the analysis. Principal Component Analysis (PCA) and Agglomerative hierarchical clustering (AHC) were used to extract from the data set the simplified dynamics behind the elements. Water samples were collected from 20 points established across the middle sector of Rebricea river for two seasons, more precisely for the months January and April. The evaluation follows the European Community Water Framework Directive (European Commission, 2000), by the category of elements selected and which are transposed in National legislation through HG 1038/2010. The physicochemical elements taken into consideration for this study are: thermal condition (temperature of water and conductivity), acidification status (pH and total alkalinity), oxygenation conditions (dissolved oxygen) and nutrients (N-NO_3^-, N-NO_2^-, N-NH_4). These parameters were determinate in situ or after the samples were stored in a refrigerator at 4°C prior to the analysis in the laboratory (the chemical parameters) using methods as colorimetry and spectrophotometric method with Shimadzu 1601; at 415 nm for nitrates and 430 nm for ammonium.

3 RESULTS AND DISCUSSION

Water temperature is an important parameter which influences the chemical process such as dissolution-precipitation, adsorption–desorption, oxidation–reduction and physiology of biotic community in an aquatic habitat (Aken 2008). It varies in situ on winter between 1-4°C accordingly with the river morphometry course, the higher values being representative for downstream, being maintained in the spring; the values range between 6-12°C it is influenced also by the spring runoff regime representative for the study area. The moment of sampling is important to mention because parameters are influenced by the local environment condition. Temperature variation influences directly the other following three parameters (pH, DO and EC) and all of biotic cycles of this microsystem.

The measurements of pH 7.08 – 8.05 includes the water body in a neutral class, the outlier value is 6.58 pH units recorded in January (Fig.2). Variation of pH are noted in the daytime and spring; as main factors are mentioned photosynthesis and respiration of local flora and fauna as well as the rainfall that took place two days before sampling in April.

Dissolved oxygen (DO) in water is explained through two natural processes: (1) diffusion from the atmosphere and (2) photosynthesis by aquatic plants. Concentrations of water samples are at relatively low rates 2.66 - 6.90 mg/l with a 5.46 mg/l average in winter and 4.70 mg/l in spring. These parameters are the results of rainy spring period and may also indicate chemical oxidation or an excess amount of biological oxygen demand based on organic discharges.

Electrical conductivity (EC) estimates the amount of total dissolved salts (TDS), or the total amount of dissolved ions in the water. The average values for these two seasons are 859.55 µS/cm and 917.35 µS/cm. For the spring time it is observably the uniformity of the data values and the main causes are morphology and topo climate of the study area.

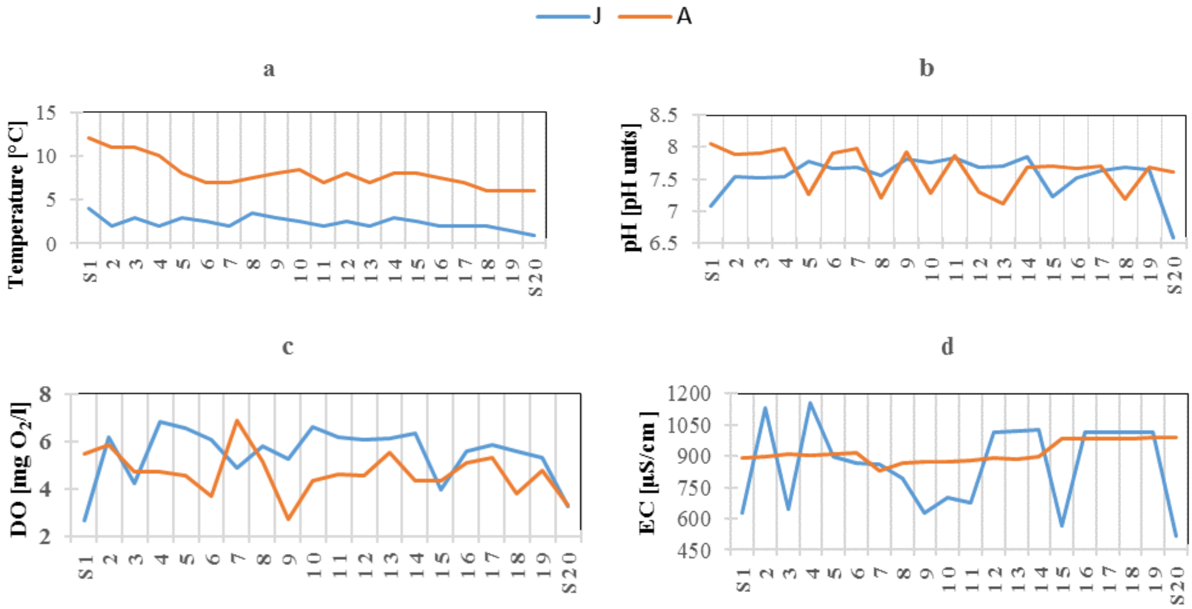

Figure 2. Seasonal parameters variation in middle sector of Rebricea river (a-temperature in situ, b-pH, c-Dissolved Oxygen, d-Electrical Conductivity)

In nutrients case, for this preliminary study were selected three parameters. Nitrates have been identified in all samples, the maximum allowed concentration of 50.0 mg/l not being surpassed (Table 1). For the second parameter, nitrites, traces were not present in the water samples study. Ammonium presence in water is due to incomplete degradation of organic substances containing nitrogen or it may originate from soil, as a result of inappropriate agricultural techniques made upon the fields (Vasiliniuc and Hutupasu, 2011).

Table 1. NO_3 and NH_4 main statistical values

	Minimum	Maximum	Mean	Standard deviation
NO_3 January	0.066	0.210	0.098	0.038
NO_3 April	0.070	0.089	0.085	0.004
NH_4 January	0.533	2.680	1.373	0.701
NH_4 April	0.346	3.248	1.623	0.906

The Table 2 and 3 are indicating values of the eight principal components and their correlation matrix calculated with Pearson (n) method. This method provides a statistical review of the influences that parameters have on each other. In this case it is easy to comprehend the role of the elements in future evolution of the river characteristic and if human activities can modify these cycles.

Table 2. Physical-chemical parameters in January (Correlation matrix (Pearson (n))

Variables	DO	Temp.	EC	pH	NO_3	NH_4	KH	GH
DO	**1**							
Temp.	**-0.826**	**1**						
EC	**0.665**	**-0.573**	**1**					
pH	**0.781**	**-0.520**	0.470	**1**				
NO_3	-0.263	0.147	-0.127	-0.168	**1**			
NH_4	-0.003	-0.062	0.079	-0.067	**0.710**	**1**		
KH	-0.327	0.134	-0.257	-0.364	0.085	0.035	**1**	
GH	-0.196	0.199	0.414	-0.205	0.079	0.063	0.161	**1**

Table 3. Physical-chemical parameters in April (Correlation matrix (Pearson (n))

Variables	DO	Temp.	EC	pH	NO_3	NH_4	KH	GH
DO	**1**							
Temp.	0.028	**1**						
EC	-0.296	-0.424	**1**					
pH	0.101	0.271	-0.084	**1**				
NO_3	-0.296	-0.034	-0.102	-0.323	**1**			
NH_4	0.088	**0.456**	**-0.745**	0.035	0.158	**1**		
KH	0.359	0.062	0.004	0.045	-0.049	0.025	**1**	
GH	0.377	**-0.597**	0.254	-0.020	-0.157	-0.087	0.231	**1**

For January are identify high correlations between three variables: dissolved oxygen, pH and temperature with values from -0.826 to 0.781; for the first case, dissolved oxygen and temperature are in negative correlation - when the temperature is high the concentration of DO are low. For nitrates and ammonium, the correlation is 0.710, each of the parameter recordings with direct proportionality of values. The next data set is defined mainly by negative correlations, evidencing a weak relationship between variables. For example, if changes occurred in total alkalinity (KH) they are not correlated with changes in the electrical conductivity (EC 0.004), but values over (-)0.5 are present for temperature, total hardness (GH), electrical conductivity (EC) and NH_4 (ammonium). In April all correlations are below 0.5, temperature has the closest value reported at EC and NH_4; negative correlations are identified between temperature and total hardness (-0.597), electrical conductivity and nitrates (-0.745). The lowest significant value of the correlation is 0.004 identified for the relation between electrical conductivity (EC) and total alkalinity (KH).

Principal Component Analysis (PCA) technique emphases variation and brings out strong patterns in dataset. In this case, the eigenvalues ratio is the ratio of explanatory importance of the factors with respect to the variables. Three principal factors were identified for each study month. For January, F1 shows maximum loadings among DO, pH and EC, F2 is defined by NO_3 and NH_4, maximum values for GH made it the F3. The F1 and F2 explain 60.87 % of the total variance followed by 16.41 % of F3. These relations between parameters are displayed in Figure 3 (a, b and c), the four quadrant are unevenly represented by the values of each element taken in consideration. F 1 had high positive loading from dissolved oxygen, pH and electrical conductivity, and a negative one for temperature.

The correlations between variables and factors of April are shown in Figure 3 (d, e, f) and are more equally scattered in the quadrants. It is visible the direct or inverse relations among the all eight analyzed parameters. In this case, F1 is defined by thermal conditions, F2 by oxygenation conditions and F3 acidification status (pH). The first two explains 52.26 % while F3 has 16.72 % from total variance and a negative loading for temperature (- 0.082) into the statistically significant clusters.

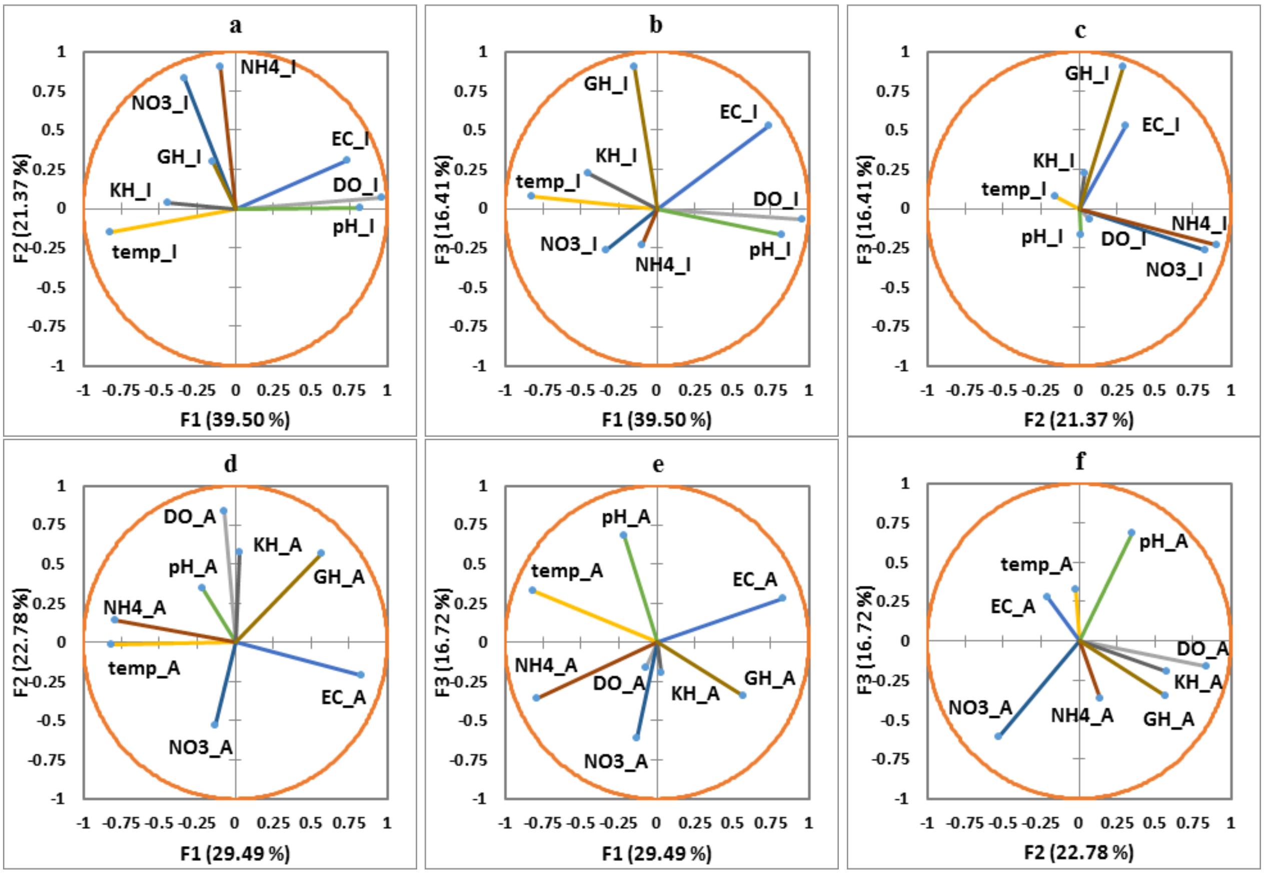

Figure 3. Correlation between variables and factors (January a: F1-F2, b: F1-F3, c: F2-F3; April d: F1-F2, e: F1-F3, f: F2-F3)

For better understanding of data, Table 4 is preceded by Agglomerative hierarchical clustering (AHC) using the Ward's method which presents data by two statistically significant clusters (Figure 4). The horizontal dashed line represents the calculated point of separation of the two main groups of indices and the dissimilarity value is 70669.80. The data emphasize the two major clusters based on dissimilarity values. The first cluster is formed by samples 1, 3, 9, 10, 11, 15, 20, the second cluster contains samples 2, 4-8, 12-14, 16-19.

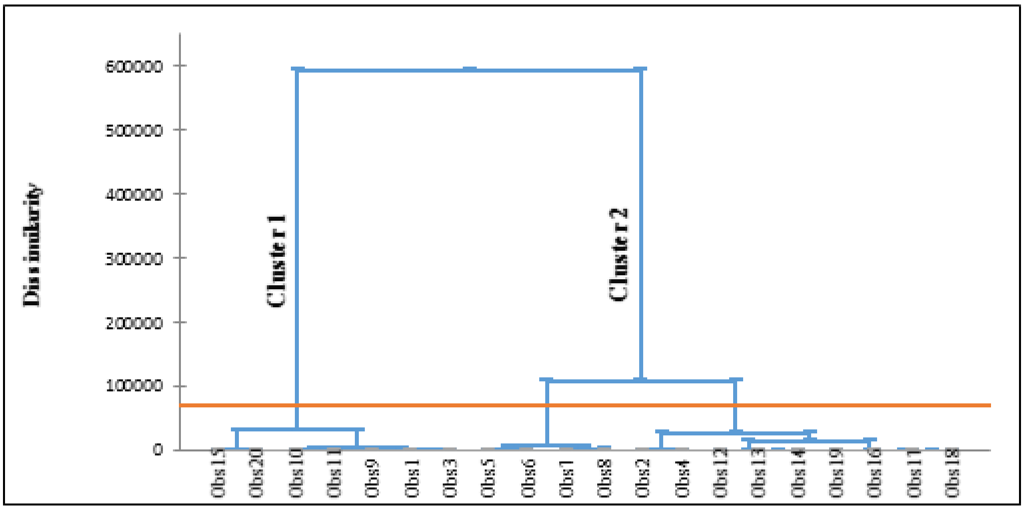

Figure 4. Dendrogram of the cluster analysis according to the 20 sampling points of the Rebricea river middle basin

Factor scores is a composite measure made for every observation for the sampling. Table 4 shows the manner how each factors influence each water samples. Each row has recorded the number of sample point and its correspondent value of factor score. The arrow suggests the direction of growing values from the negative to positive ones. In this case the principle of correlation is applied, negative values suggest that for the sampling point F1, F2 or F3 have an inverse influence. Positive values suggest that between the sampling point and the specific factor there is a direct influence. For the first month, the lowest rate of factor score is -4.48 in sample 1 for F1 (dissolved oxygen, pH and electrical conductivity) and the highest 2.81 in sample 4 for F2 (NO_3 and NH_4). The scores for April range between -2.63 ÷ 2.70 for the same factor F1 (electrical conductivity) in samples 4 and 17. Sample 1 is again present by having the highest value for F2 (2.59) and Sample 9 -1.98. The data for F3 oscillate from -2.39 to 2.12 in Sample 13 and 17 opposing the range of -1.98 to 2.49 from January.

Table 4. Factor scores values of Rebricea middle river basin for months January and April

January						**April**					
Sample	**F1**	**Sample**	**F2**	**Sample**	**F3**	**Sample**	**F1**	**Sample**	**F2**	**Sample**	**F3**
Sample 1	-4.48	*Sample 20*	-1.84	*Sample 11*	-1.98	*Sample 4*	-2.63	*Sample 9*	-1.98	*Sample 13*	-2.39
Sample 20	-3.86	*Sample 15*	-1.34	*Sample 10*	-1.81	*Sample 3*	-2.27	*Sample 20*	-1.92	*Sample 12*	-1.62
Sample 15	-2.62	*Sample 11*	-0.99	*Sample 9*	-1.35	*Sample 10*	-1.75	*Sample 18*	-1.73	*Sample 8*	-1.31
Sample 3	-1.73	*Sample 9*	-0.99	*Sample 8*	-1.01	*Sample 9*	-1.71	*Sample 5*	-1.56	*Sample 10*	-1.13
Sample 9	-0.88	*Sample 18*	-0.95	*Sample 5*	-0.94	*Sample 7*	-1.21	*Sample 19*	-1.27	*Sample 14*	-0.89
Sample 7	-0.35	*Sample 19*	-0.78	*Sample 3*	-0.89	*Sample 12*	-0.71	*Sample 6*	-1.22	*Sample 18*	-0.74
Sample 8	-0.06	*Sample 10*	-0.78	*Sample 6*	-0.81	*Sample 11*	-0.56	*Sample 10*	-1.16	*Sample 11*	-0.73
Sample 17	0.28	*Sample 6*	-0.74	*Sample 20*	-0.20	*Sample 13*	-0.52	*Sample 12*	-0.62	*Sample 16*	-0.57
Sample 2	0.51	*Sample 12*	-0.67	*Sample 7*	0.05	*Sample 8*	-0.42	*Sample 11*	-0.05	*Sample 15*	-0.11
Sample 18	0.73	*Sample 14*	-0.63	*Sample 19*	0.09	*Sample 2*	-0.37	*Sample 14*	0.16	*Sample 7*	0.02
Sample 16	0.81	*Sample 16*	-0.58	*Sample 14*	0.09	*Sample 6*	-0.18	*Sample 4*	0.17	*Sample 5*	0.13
Sample 19	0.82	*Sample 13*	-0.54	*Sample 1*	0.09	*Sample 1*	-0.04	*Sample 3*	0.44	*Sample 1*	0.18
Sample 13	1.03	*Sample 17*	-0.39	*Sample 12*	0.14	*Sample 5*	-0.01	*Sample 15*	0.49	*Sample 2*	0.35
Sample 10	1.07	*Sample 7*	0.48	*Sample 4*	0.44	*Sample 14*	0.10	*Sample 8*	0.68	*Sample 19*	0.50
Sample 11	1.15	*Sample 8*	0.71	*Sample 2*	0.45	*Sample 19*	1.48	*Sample 13*	0.77	*Sample 20*	0.72
Sample 6	1.15	*Sample 3*	1.14	*Sample 15*	0.82	*Sample 20*	1.55	*Sample 16*	1.07	*Sample 9*	0.93
Sample 12	1.42	*Sample 5*	1.45	*Sample 18*	1.11	*Sample 16*	2.04	*Sample 2*	1.26	*Sample 3*	1.37
Sample 4	1.55	*Sample 1*	2.25	*Sample 16*	1.61	*Sample 15*	2.13	*Sample 17*	1.80	*Sample 6*	1.43
Sample 14	1.72	*Sample 2*	2.38	*Sample 13*	1.63	*Sample 18*	2.37	*Sample 7*	2.09	*Sample 4*	1.73
Sample 5	1.73	*Sample 4*	2.81	*Sample 17*	2.49	*Sample 17*	2.70	*Sample 1*	2.59	*Sample 17*	2.12

4 CONCLUSIONS

This preliminary study indicates a good state of Rebricea water quality for the selected seasons based on analysis of principal components. Other important variables worth mentioned are human pressure, geomorphology of the area, the presence of stationary vegetation, and the characteristics of land use and water management plan and of sampling on the other hand. The statistical methods offer a way to estimate sources contribution, which are useful for refining parameters inventor. In this particular case, temperature, dissolved oxygen and pH are defining parameters for water samples.

Based on PCA results it can be noted that from eight chosen parameters, the characteristics of the surface water can be determined by three factors that cumulated 77.28 % of the total variance for January and 68.98 % for April. The factor scores and dendrogram established that the parameters are placing the river at the "good" state quality accordingly with the reports given by The "Romanian Waters" National Administration Prut-Barlad Branch. An extensive analysis regarding the seasonal variations of parameters will be made within the doctoral research years.

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