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Assessment of the Water Quality Index in the Semani River in Albania

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Abstract

Nowadays the human activity has increased the pressure on surface water quality. The purpose of this study is to assess the environmental quality of the Seman River water (in Southern part of Albania) through a 5-year monitoring program of 14 parameters (pH, DO, EC, TSS, Cl^-, NO_3^-, Total-N, Total-P, BOD_5, Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} and Temp. ˚C), that determine the environmental status of this waterbody, as well as the application of WQI (CCME) through a multivariable approach. Based on the cluster dendogram results, it can be concluded that during wet seasons such as winter-spring, there are more sediments which influence other physic-chemical parameters, while during dry seasons (summer-autumn) there are more decomposition reactions of elements released by sediments and influenced by temperature. PCA analysis determines whether the groups of factors correlate strongly or not, depending on the internal structures of the groups and variables "heavy" or latent and vary from season to season with differentiated contributions to the water quality. All three factors influence WQI to the extent of 56% in the summer and spring season and 64% and 40% in the autumn and winter season, respectively.

Keywords

Cluster, PCA (Principal Component Analysis), Physicochemical Parameters, Seman River, WQI (Water Quality Index)

1. Introduction

The abundance of rivers and the dense network of surface waters in Albania are a national wealth which is under threat by increased human pressure. The rivers provide several ecological services including regulation of hydrological balance of potable water, as well as usages in agriculture, recreation, aquaculture, hydropower and industry [1]. The deterioration of riverine waters is caused by several factors including climate, hydrology, vegetation cover, land use, geology, topologic and geographic features, and of course the ever-expanding anthropogenic factors. The main anthropogenic sources of pollution may be grouped as: 1) erosion from barren lands; 2) runoff and infiltration from waste deposit/treatment, mines and oilfields; 3) industrial wastewater effluents; 4) agricultural activities; and 5) overflow from combined and sanitary sewers [2] [3] [4] [5] [6]. The hydrology plays an essential role in the dispersion of pollutants and their retention in the riverine ecosystem depends on the residual time and contact with the surface. Due to favorable hydrologic conditions, the lower part of the rivers, lagoons and riparian zone was identified as essential sinks for river basin [7]. Human activity has fundamentally altered the cycles of soluble pollutants by increasing their transfer across rivers to coastal waters, deteriorating the quality of their waters and affecting even transnational waters [8] [9]. Considering that water pollution and its irrational use represent two risk factors for the sustainable development of human society, constant monitoring of water quality is important. Natural and anthropogenic processes determine the chemical composition in surface waters [10]. Preservation of environmental water quality is achieved through the definition of indicators that are monitored and specific to freshwater. There are a number of indicators that represent different aspects of water quality that vary in their significance in different geographical regions [11]. Furthermore, it may be difficult to convey relevant water quality information to policymakers and the public [11]. There are a number of indices used to assess water quality based on physical, chemical or biological parameters separately. The history of the development of these indices is discussed by many authors [12] [13] [14] [15] [16]. Water monitoring management for a long period of time at many points offers a wide and complicated range of data of physic, chemical and biological water parameters which, not only are difficult to analyze and interpret, but also extract comprehensible information for decision makers [17]. A number of special software-based methods and guidelines have been developed in recent decades [18]. The methods generally tend to group the data according to the source origin and their impact on water quality by identifying the trend, their weight, prioritizing the impact of a set of factors and the response of the aquatic ecosystem for adaptation or not. Water quality index (WQI) was developed to become a tool to simplify the reporting of water quality data [19]. As a summary tool, it provides a broad overview of water quality data and is not intended to be a substitute for detailed analysis of water quality data [20]. The application of different multivariate approaches (cluster analysis, principal component analysis, factor analysis and discriminant analysis) helps in the interpretation of complex data matrices, provides a better indication of water quality and ecological status of the studied systems, allows for the identification of possible factors/sources that affect water bodies, provides a valuable tool for reliable management of water resources, and finally offers a rapid solution to the pollution problem [21] [22] [23]. Albania has revisited the environmental laws. The 2011 Law on Environmental Protecton [24] and the standards for freshwaters are very similar to the EU countries (Water Framework Directive 2000/60/EEC). The major goal is to attain the same water quality indicators as EU by 2020 [25]. A surface water monitoring network has been established and every year the data of chemical, physical and biological parameters are reported [26]. However, they are still insufficient since 1) the indices are still deficient/small, 2) the frequency of sampling analysis unsuitable and 3) the sites do not cover the entire territory with the required density for an in-depth analysis of river water quality. The purpose of this study was to assess the environmental quality of the Seman River water through a 5-year monitoring program of 14 parameters that determine the environmental status of this waterbody, as well as the application of WQI [19] through a multivariable approach, specifically Cluster Dendogram and Principal Components Analyzes (PCA) [3].

2. Material and Methods

2.1. Monitoring Area

The Seman River is one of the seven most important rivers in Albania, which flows from the mountainous heights in the east and descend to the west where the coastal lowlands have created good quality land for agricultural production. It consists of two important tributaries: Devoll and Osum with a length of 281 km, basin area of 5649 km^2 and an average flow of 96 m^3/sec (**Figure 1**). The physio-geography classifies the study area as a mountainous region (>700 m above sea level) in the upstream east, with ultrabasic rocks at the source and a small population density (<50 inhabitants/km^2), and a hilly-plain region downstream mainly composed of geologically limestone, with a high population density (>200 inhabitants/km^2) and with intensive agricultural and industrial development. The Seman basin provides potable water for about 300,000 inhabitants, and irrigation water for about 55,000 hectares of land with high intensity of agricultural production. High seasonal variation of the flow in the summer period leads to lack of water for irrigation by increasing pollution pressure on the of drinking water quality. The Seman River water quality is defined as average to poor, especially due to the TSS (Total Suspended Solids) and the organic materials contained [27] [28]. The quality of water for irrigation and drinking is often questionable due to the discharge of untreated sewage from the four cities that Semani River runs through, namely Gramsh, Corovoda, Berat and Fier.

2.2. Stations and Sampling Period

Due to the complex geomorphology, six monitoring stations were defined along the middle course of the Seman River: two at the discharge of its tributaries

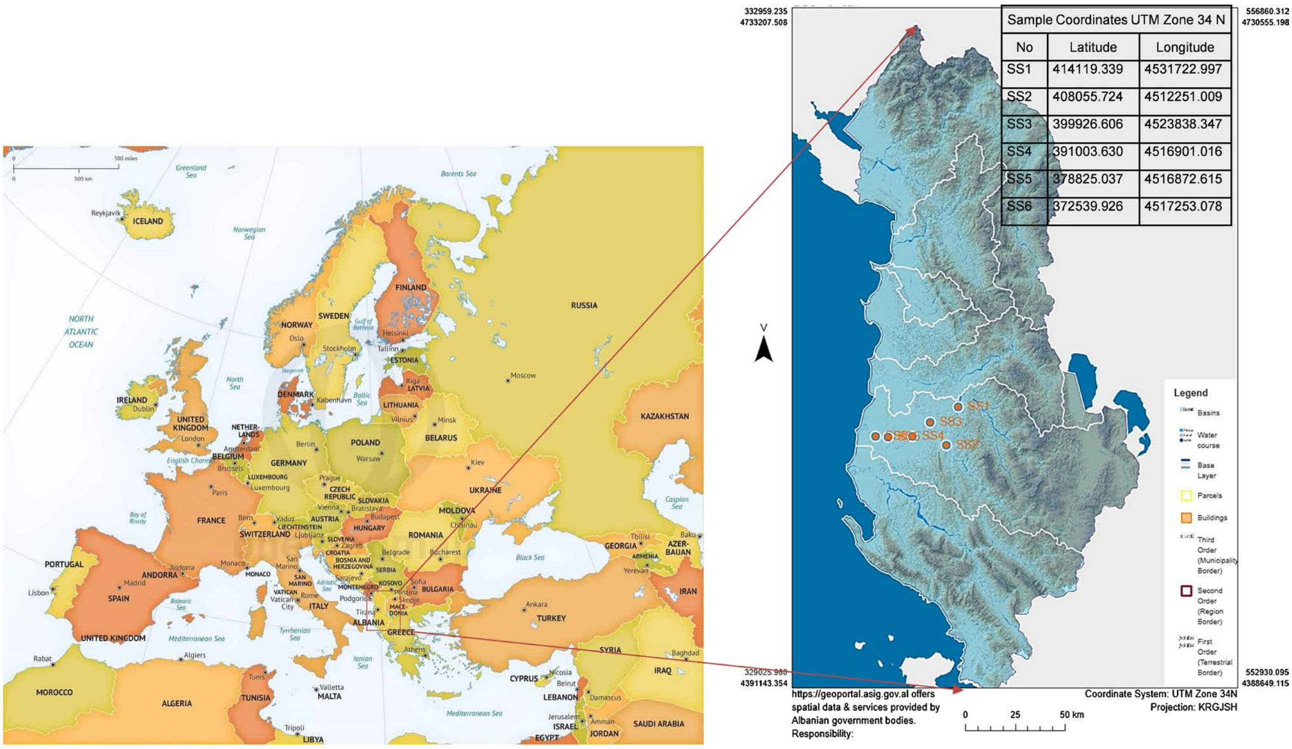

Figure 1. Sampling stations at the Seman River in Albania (Map not in Scale).

(Devoll and Osum), two in the upper stream prior to reaching the city of Fier and two further downstream, passed the city of Fier. Water sampling were performed in four seasons (spring, summer, autumn and winter) for a period of five years beginning from 2014 to 2018. The sampling stations were selected based on the expectation that water quality was modified whenever there were significant impacts through point pollution—especially from industry and untreated urban wastewater—and diffuse pollution, mainly from agriculture and erosion.

2.3. Monitored Parameters and Analytical Methods

Six water samples (pursuant the preselected sampling stations) were taken in four seasons, namely winter (January), spring (April), summer (July) and autumn (November) in 2014, 2015, 2016, 2017 and 2018, to determine the following parameters (pH, DO, EC, TSS, Cl^-, NO_3^-, Total–N, Total–P, BOD_5, Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} and Temperature ˚C). Samples were taken with plastic bottles of 1 L volume, at a depth of about 20 cm below the water surface. The bottles were stocked in freezer boxes at about 4˚C during the transport, and were taken to the laboratory where they were placed in the refrigerator at −20˚C for further analysis. Parameters such as temperature (Temp. ˚C), pH, DO (dissolved oxygen), EC (electrical conductivity), salinity and turbidity were measured *in situ* using a HANA multiprobe instrument. Analysis of the mineral forms of nitrogen and phosphorus (NO_3^-, NH_4^+ and PO_4^{3-}) were conducted based on the ultraviolet spectrophotometric screening method [29]. Determination of orthophosphate was performed according to the ammonium molybdate spectrometric method specified in standard ISO 6878:2004. Determination of mineral nitrogen forms dissolved in water, was conducted based on the manual spectrometric method ISO 7150: 1984 (for ammoniacal forms) and on the 2,6-dimethylphenol spectrometric method ISO 7890-1:1986 (for nitrates and nitrites). For the determination of DO (Dissolved Oxygen) and BOD (Biological Oxygen Demand) were used the standard methods of the American Public Health Association [30] and for the determination of heavy metals (Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}) was used a Flame Atomic Absorption Spectrometer type AA350.

2.4. Model and Statistical Analyses

The Water Quality Index (WQI) represents a numerical expression which has the purpose of establishing the ecological state of the water body. The formulation of the CCME WQI is described in the Canadian Water Quality Index 1.0 - Technical Report Principally, the model consists of three measures of variance from selected water quality objectives (Scope, Frequency, Amplitude). The "Scope (F1)" represents the extent of water quality guideline non-compliance over the time period of interest. The "Frequency (F2)" represents the percentage of individual tests that do not meet objectives. The "Amplitude (F3)" represents the amount by which failed tests do not meet their objectives. These three factors combine to produce a value between 0 and 100 that represents the overall water quality [31].

For the calculation of this index, we have considered the following parameters: temperature, pH, EC, DO, TSS, BOD, nitrogenous, nitrites, ammonium (NH_4^+), chlorine and heavy metals (Pb^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}). The WQI calculator used by us categorized water as: excellent (95 - 100), very good (89 - 94), good (80 - 88), fair (65 - 79), marginal (45 - 64), and poor (0 - 44) [19]. Cluster analysis (CA) was used to find the internal structure of a data grouped in advance based on their similarities [32]. Hierarchical Cluster is the most common approach, where clusters are formed sequentially starting by the most similar pair of objects and forming higher clusters in a step-by-step pattern, according to JUMP SAS 11 software. Principal Component Analysis (PCA) is a powerful technique used for recognition of patterns which can explain the variance of large data sets of inter-correlated variables and transform them into smaller sets of independent variables (principal components) [14]. Software used is: JMP, 11, 2014, John P. Sall, it is a trial version.

3. Results

In **Table 1**, the values of the parameters measured in the Seman River water were expressed as the average of the four sampling stations with the maximum, minimum, standard deviation and standard error values in the four seasons of the monitoring period. The letters in superscript explain the differences of seasonal averages from 2014-2018 for each measured parameter analyzed as LSMeans Differences Tukey HSD (JMP, 11), where $\alpha = 0.050$ and were levels not connected

Table 1. Values of all monitored parameters of the Semani River expressed as mean, maximum, minimum, standard deviation and standard error.

Monitoring average values of Seman sampling stations (n= 20)																						
Parameters	Unite measure	2014-2018																				WHO
		Spring					Summer					Autumn					Winter					
		$\overline{X}$	STDEV.s	SERR	Min	Max	$\overline{X}$	STDEV.s	SERR	Min	Max	$\overline{X}$	STDEV.s	SERR	Min	Max	$\overline{X}$	STDEV.s	SERR	Min	Max	
pH	UpH	7.9^a	±0.18	±0.19	7.75	8.15	7.8^a	±0.78	±0.19	6.5	8.51	8.1^a	±0.18	±0.19	7.85	8.3	8.1^a	±0.24	±0.19	7.8	8.455	6.5 - 8.5
DO	$mgO_2 \cdot L^{-1}$	8.0^a	±0.45	±0.33	7.35	8.45	7.4^a	±0.92	±0.33	6.1	8.51	7.5^a	±1.20	±0.33	5.95	8.75	7.4^a	±0.92	±0.33	6.2	8.51	7 - 14
EC	$mS \cdot cm^{-1}$	435.1^a	±102.87	±33.88	337	565.5	487.7^a	±88.14	±33.88	408	631	523.5^a	±156.68	±33.88	396.5	728	476.4^a	±84.43	±33.88	356.5	571.5	800
TSS	$mg \cdot L^{-1}$	1151.7^a	±311.22	±293.78	911.5	1569	646.1^a	±149.90	±293.78	462.5	853.5	1169.7^a	±984.37	±293.78	620.5	2918	1502.5^a	±810.96	±293.78	801.5	2881.5	30 - 200
Cl^-	$mg \cdot L^{-1}$	32.1^b	±5.01	±7.08	26.3	38.5	56.5^a	±25.56	±7.08	32.5	90	38.9^{ab}	±11.57	±7.08	26.5	54	50.7^{ab}	±26.54	±7.08	30	96.5	200 - 500
NO_3^-	mgL^{-1}	0.9^a	±0.46	±0.23	0.3	1.3	1.1^a	±0.51	±0.23	0.4	1.6	1.1^a	±0.43	±0.23	0.65	1.8	1.5^a	±0.84	±0.23	0.6	2.68	1 - 11.3
Total-N	$mg \cdot L^{-1}$	1.4^a	±0.82	±0.39	0.4	2.55	1.6^a	±1.01	±0.39	0	2.55	1.9^a	±0.91	±0.39	1.1	3.35	1.9^a	±1.19	±0.39	0.61	3.6	1.5 - 20
Total-P	$mg \cdot L^{-1}$	0.7^a	±0.42	±0.12	0.2	1.14	0.7^a	±0.37	±0.12	0	0.94	0.7^a	±0.21	±0.12	0.3	0.8	0.7^a	±0.25	±0.12	0.22	0.87	0.1 - 1
BOD_5	$mgO_2 \cdot L^{-1}$	20.9^a	±14.26	±4.41	0	37	25.4^a	±16.46	±4.41	0	40.5	24.0^a	±8.23	±4.41	13.5	34	30.2^a	±15.32	±4.41	18	52.5	3 - 7
Cu^{2+}	$\mu g \cdot L^{-1}$	0.2^a	±0.09	±0.04	0.16	0.36	0.3^a	±0.12	±0.04	0.11	0.41	0.3^a	±0.15	±0.04	0.14	0.51	0.3^a	±0.09	±0.04	0.15	0.38	3
Ni^{2+}	$\mu g \cdot L^{-1}$	0.6^a	±0.34	±0.29	0.07	0.96	0.7^a	±0.78	±0.29	0.02	1.5	0.3^a	±0.62	±0.29	0.02	1.45	0.8^a	±0.82	±0.29	0.06	1.76	8
Pb^{2+}	$\mu g \cdot L^{-1}$	2.2^b	±1.09	±0.4	0.9	3.53	1.6^b	±1.07	±0.4	0.6	3.205	1.7^b	±0.83	±0.4	0.77	2.735	4.5^a	±1.35	±0.4	2.75	6.12	2.5
Cd^{2+}	$\mu g \cdot L^{-1}$	0.5^a	±0.52	±0.17	0.05	1.25	0.6^a	±0.45	±0.17	0.06	1.17	0.5^a	±0.38	±0.17	0.1	0.94	0.8^a	±0.48	±0.17	0.15	1.31	0.2 - 1
Temp.	˚C	14.9^{bc}	±0.64	±0.68	13.9	15.4	22.8^a	±0.52	±0.68	22	23.25	16.5^b	±1.37	±0.68	14.8	18.3	13.6^c	±3.10	±0.68	10.45	18.2	5.0 - 28

by the same letter are significantly different. The variation of values is higher between seasons compared to the variations between sampling points. pH values fluctuate between 7 and 8, higher in autumn and winter compared to the other two seasons. Dissolved oxygen (DO) values have a maximum during the spring season 8.0 and about 7.5 during the other three seasons, while the minimum and maximum values of BOD_5 ranged from 20.9 and 52.5. The range of electrical conductivity EC values is between 430 mS·cm^{-1} in spring and 523 mS·cm^{-1} in autumn. The minimum and maximum values of TSS ranged from 641 mg·L^{-1} in summer to 1502.5 mg·L^{-1} in winter; for Total-N dissolved values ranged from 1.4 mg·L^{-1} to 1.9 mg·L^{-1}, respectively; for Total-P values ranged from 0.2 to 1.13 mg·L^{-1}, while the mean was the same for all seasons; for NO_3^- values ranged from 1.6 mg·L^{-1} in spring and 3.6 in winter; and for Cl^- values ranged from 26 mg·L^{-1} in spring and 96.5 mg·L^{-1} in winter. Heavy metal values expressed in µg L^{-1} ranged between 0.2 - 0.3 for Cu^{2+}; 0.3 - 0.8 for Ni^{2+}; 1.6 - 4.5 for Pb^{2+}; and 0.5 - 0.8 for Cd^{2+}.

4. Discussions

Average values for the whole study period were compared with WHO thresholds referring to surface water quality in agricultural, industrial and urban areas (Figure 2). The values of NO_3^-, Total-N, Total-P, Cu^{2+}, Ni^{2+} and Cd^{2+} were much lower than the WHO threshold values. The values for pH, EC, Cl^- and temperature were also lower than thresholds, while the values for DO varied and were very close to the threshold values, albeit sometimes higher than the threshold values. The values of TSS and BOD_5 were higher than the threshold values. The values of TSS and BOD_5 were higher than the threshold values.

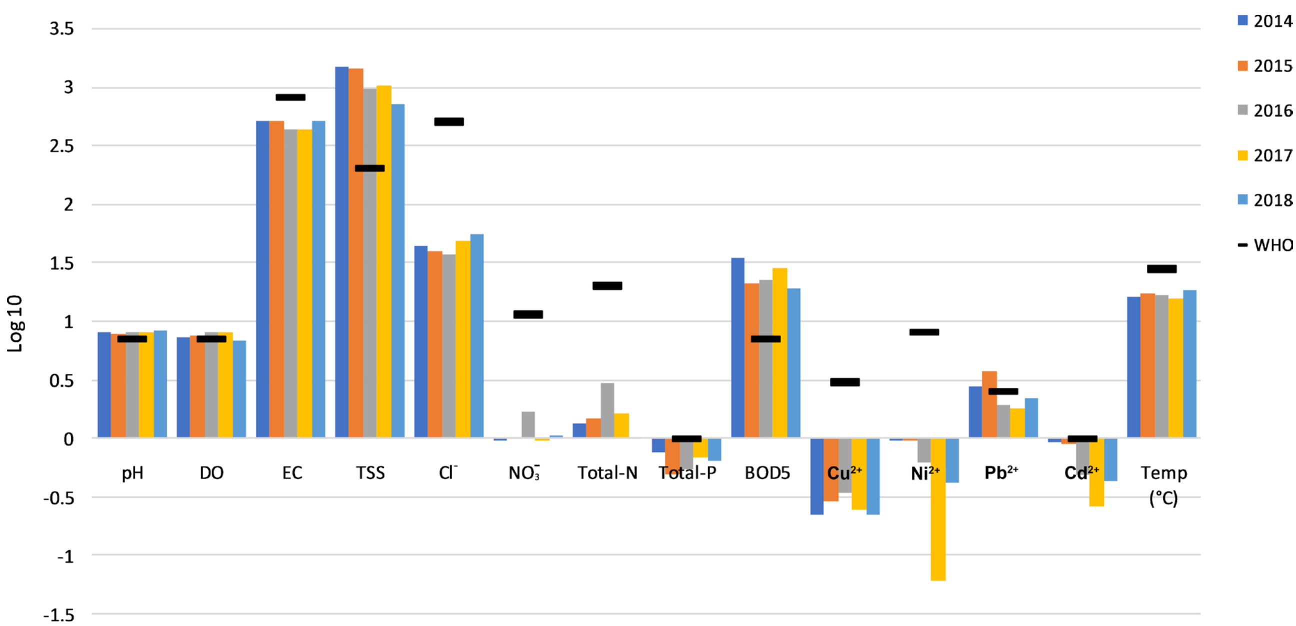

Figure 2. Comparison between the average values of the monitored parameters at the Seman River and the WHO threshold values.

4.1. Water Quality Characteristics Based on the Water Quality Index

For all seasons in five years, the value of WQI fluctuates between 55% and 86% with variations between years and seasons (**Figure 3**). Except for the autumn 2014, all downstream values were higher compared to the upstream ones due to the impact of untreated sewage and industries present in Fier city, the largest one amongst the cities where Seman River flows. However, the largest differences between the average values of WQI in the upper and downstream were observed in the spring and winter seasons, which are rainy seasons affecting the transport of urban and industrial wastes to the river, the erosion of agricultural land, and the transport of agricultural fertilizers, especially Total-N and Total-P.

The average values of downstream stations based on WQI can lead to a possible explanation of the water degradation, visible mainly in the deteriorated values of TSS, BOD_5, DO and EC. All these parameters are determined mainly by human activity due to the release into the river of solids of mainly organic nature, which is evidenced mainly by the high biological demand as well as by the low values of dissolved oxygen. Cluster analysis weight groups of parameters by revealing the internal structure of a parameter compared to other parameters by grouping these according to the "weight" they have in water quality, always compared to the threshold values. Below are the dendograms of the four seasons, where the clusters (**Figure 4**) present the groups of the monitored mean values and relationships between them for the following parameters pH, DO, EC, TSS, Cl^-, NO_3^-, Total-N, Total-P, BOD_5, Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} and Temp. ˚C. At Cluster 1 during the Autumn seasons (2014-2018) (**Figure 4(a)**), the parameters are classified in eight groups, where the most important ones are ranked as follows: pH linked with DO, EC, NO_3^-, Cl^-; the second group NO_3^- linked with Total-N and Total-P; the third group Total-P linked with Cu^{2+} and Cd^{2+}; and the fifth group $BOD_{5,}$ TSS and EC linked with Temp. ˚C, heavy metals and macronutrients. At Cluster

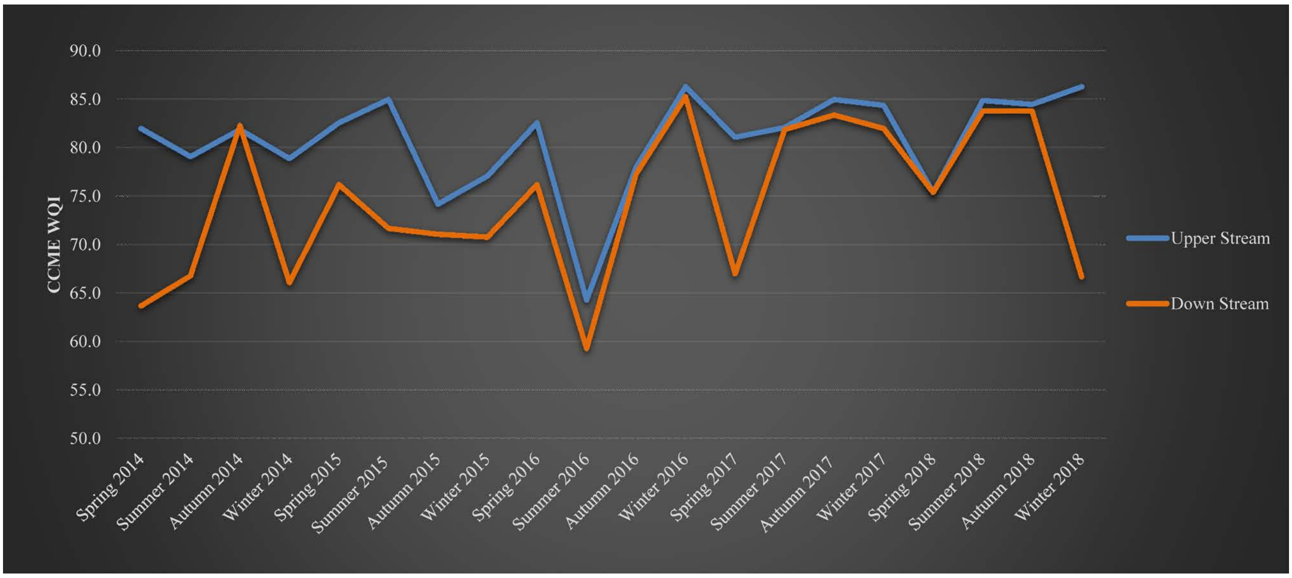

Figure 3. The sesional variation of average values of WQI in the upper and downstream of Seman River.

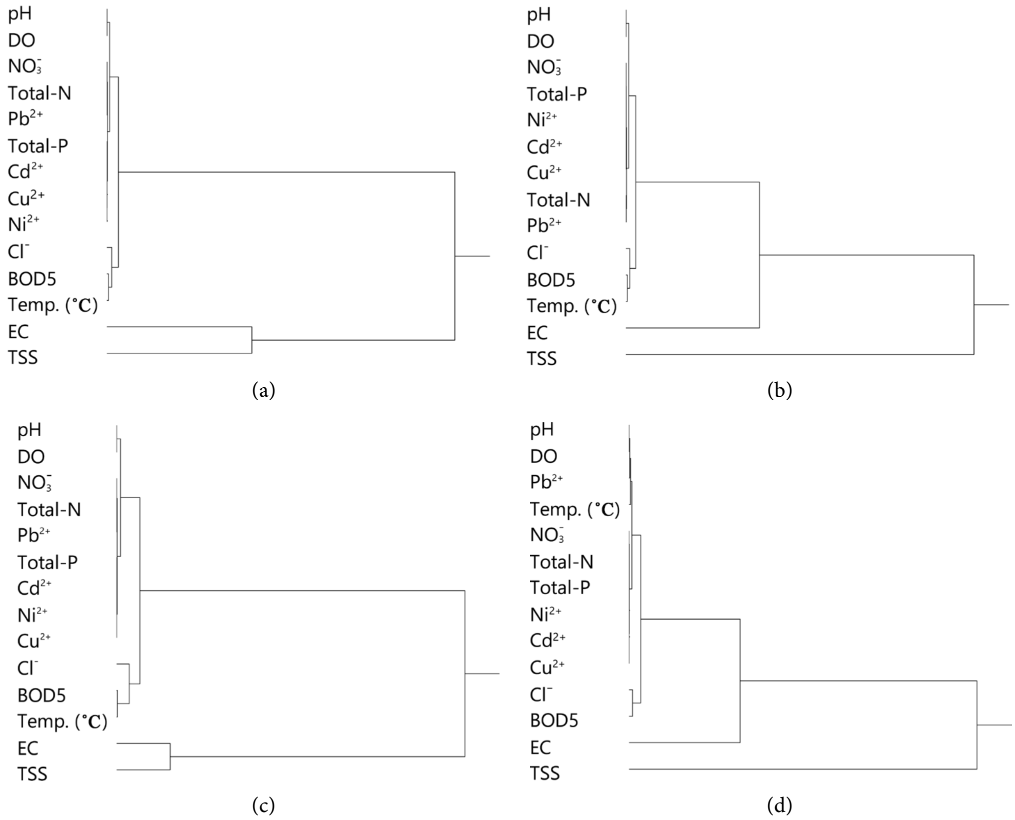

Figure 4. Seasonal Dendrograms of hierarchical clustering (Method – Ward). (a) Autumn; (b) Spring; (c) Summer; (d) Winter.

2 during the Spring seasons (2014-2018) (Figure 4(b)), the parameters are classified in seven groups, starting with pH which is linked to TSS, DO, EC, NO_3^- and Cl^-, then with the second group NO_3^- which is influenced by Total-N, Total-P and Cu^{2+}. A link between Cd^{2+} and Ni^{2+} is noted in the group of five average values. The creation of two large groups in the cluster shows that EC, Temp. ˚C, macro and microelements together are influenced by TSS as a physical indicator of the presence of suspensions in the Seman water system. Cluster 3 during the Summer seasons (2014-2018) (Figure 4(c)) the parameters are classified in seven groups starting with pH which is linked with DO, EC, NO_3^-, Cl^-, then with the second group NO_3^- which is linked with Total-N and Total-P, continuing with the third group where is a link between Total-P with Ni^{2+}, Cu^{2+} and Cd^{2+}. The groups and links are similar to the autumn season and more distanced to the spring season, with a high intensity of rain showers and with a stream flux similar to autumn. There is a similarity to autumn season with respect to the division of two major groups, where TSS and EC influence the groups of macro and microelements, as well as the pH in the Seman River water system. At Cluster 4 during the Winter seasons (2014-2018) (Figure 4(d)) the parameters are classified in four groups, starting with the first one that includes the pH which is linked with DO, NO_3^-, Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+}, Total-N, Total-P and Temp. ˚C; in the second group the first group elements are linked with Cl^- and BOD_5;

and in the third group there is a link between second group parameter results correlated with EC, TSS. The two major groups in the cluster indicates that there is a similarity to all cluster results—EC, macro and microelements, are altogether influenced by TSS, as a physical indicator of the presence of suspended solids in the Seman River waterbody.

As a result of the hierarchical CA applied in the analysis of seasonally ranked data as an average of 5 years (2014-2018), the dendrogram (**Figure 4**), refers that in the autumn and summer seasons, the relationship between Electrical Conductivity (EC) and Total Soluble Solids (TSS) is close and matched into one category. It is different for winter-spring seasons where TSS forms a category and influences all other measured physic-chemical parameters, due to the high presence of sediments through precipitation in this period and as a result of redox reactions that occur, influenced also by water temperature. Based on the results, it can be concluded that during wet seasons such as winter and spring, there are more sediments which influence other physico-chemical parameters, while during dry seasons (summer and autumn) there are more decomposition reactions of elements released by sediments and influenced by temperature.

4.2. Principal Component Analysis (Varimax Rotation)

The Principal Component Analysis (PCA) is a technique for explaining changes in data sets and the interrelationship of variables and their significance across the classified groups by "pressuring" the least influential variables. In other words, PCA reduces the impact of some variables and identifies other variables that are unobservable, hypothetical, or latent. The analyzed diagrams highlight a clear pattern regarding how parameters or variables affect each other. PCA was applied by processing the data of each season in each year studied. The PCA method is based on the study of correlation groups using Pearson distribution with the Varimax rotation method which consists of linking and directing factors to the original variables for easier interpretation. **Figure 5(a)** shows the results obtained from the PCA analysis of the measurements performed during the spring seasons from 2014-2018 which are grouped in Factor 1 which includes Cl^-, BOD_5, Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, which do not correlate with CCME WQI. This factor does not show a significant correlation and is seen to be opposite to the vertical axis (Factor 1). The second group consists of TSS, Cu^{2+}, DO which do not correlate either with CCME WQI or Ni^{2+}, BOD_5, Total-P, Total-N, NO_3^-, (Factor 2) as they are located in different axes and are not close to each other to be called as influential of each other. In the third group the strong connection of CCME WQI with pH and temperature is noticed (Factor 3). In a general view we can say that CCME WQI also links to metals like Ni^{2+}, Pb^{2+} and Cl^-, but it has an extremely small bond with BOD_5, Cd^{2+}, DO, Total-P, Total-N, and NO_3^-. All three factors explain over 56% of the total variation. The results of PCA analysis in **Figure 5(b)** in the summer season shows three groups with respective links between them. The first group includes DO, Temp. ˚C, Cl^-, NO_3^-, Total-N, Total-P and BOD_5 which do not correlate with CCME WQI. The second group includes TSS, pH which correlate strongly with CCME WQI and the third group includes mainly metals Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} which do not correlate with CCME WQI. From the comparison of F1 vs. F3 the formation of three groups is observed where the first group include DO, Temp. ˚C, NO_3^-, Total-N, Cu $^{2+}$ and Total-P, which do not correlate with CCME WQI, the second group include pH, TSS, Cl^- which correlate closely with CCME WQI and the third group is composed by heavy metals such as Ni^{2+}, Pb^{2+}, Cd^{2+} and BOD_5. From the comparison between F2 and F1 are observed two main groups such as NO_3^-, Total–N, DO, Temp. ˚C which correlate with Total-P, BOD_5 and Cu^{2+}; and Ni^{2+}, Pb^{2+}, Cd^{2+}, pH, TSS which correlate with CCME WQI except Cu^{2+} which does not correlate with any of the groups. All three factors explain over 56% of the total variation. Unlike the data recorded during the spring and summer seasons, the data collected during the five autumns of monitoring activities illustrate slightly different correlations (**Figure 5(c)**). PCA analysis in F1 vs. F2 pointed out that there is a correlation between CCME WQI and chemical parameters such as: Total Total-N, NO_3^-, pH, BOD_5, but a weak correlation with the other two groups formed on both sides of the Y axis. In the second group there is a correlation between Temp. ˚C, Cl^-, Cd^{2+} and in the third group is a correlation between Ni^{2+}, DO, Total-P, TSS, Cu^{2+}, Ni^{2+}, Pb^{2+}. The comparison between F1 and F3 highlighted two main groups where in the first group there is a correlation between DO, TSS, NO_3^-, Total-N, Total-P, Cu^2, Pb^{2+}, Ni^{2+}, in the second group there is a correlation between Cd^{2+}, Temp. ˚C, Cl^- with CCME WQI. Parameters such as pH and BOD_5, do not correlate in this comparison with any of the groups standing on the Y-axis. The comparison between F2 and F3 indicate the formation of four groups of parameters where in the first group are BOD_5 with Cd^{2+}, in the second group there is a correlation of CCME WQI with NO_3^- and Total-N, in the third group there is a correlation of Temp. ˚C with Cl^-, Ni^{2+}, pH and Cu^{2+}, and in the fourth group there is a correlation between Total-P, DO, TSS, Pb^{2+}. All three factors explain over 64% of the total variation. The winter period results in different "weight" relationships (**Figure 5(d)**) compared to the three seasons above. When comparing the factors F1 and F2 two main groups have established correlative links. In the first group there is a correlation between CCME WQI with pH, Cd^{2+}, Temp. ˚C, Cl^-, and in the second group indicates a link of Cu^{2+}, Ni^{2+} with DO and weaker with TSS, Pb^{2+} and Total-P. Three parameters do not correlate with any of the groups and they are NO_3^-, Total-N and BOD_5, thus forming a separate group. The comparison between F1 and F3 factors highlight the formation of correlation links in the first group where are included NO_3^-, Total-N, DO, TSS, Cu^{2+}, Ni^{2+}, Pb^{2+}. The formation of the second group indicates a link between CCME WQI and Cd^{2+}, Temp. ˚C, Cl^-. However, it can be noted that Total-P, BOD_5, and pH do not correlate with any of the groups. The comparison between F2 and F3 factors indicates weak correlation between parameters, and the closest link with CCME WQI is from NO_3^- and

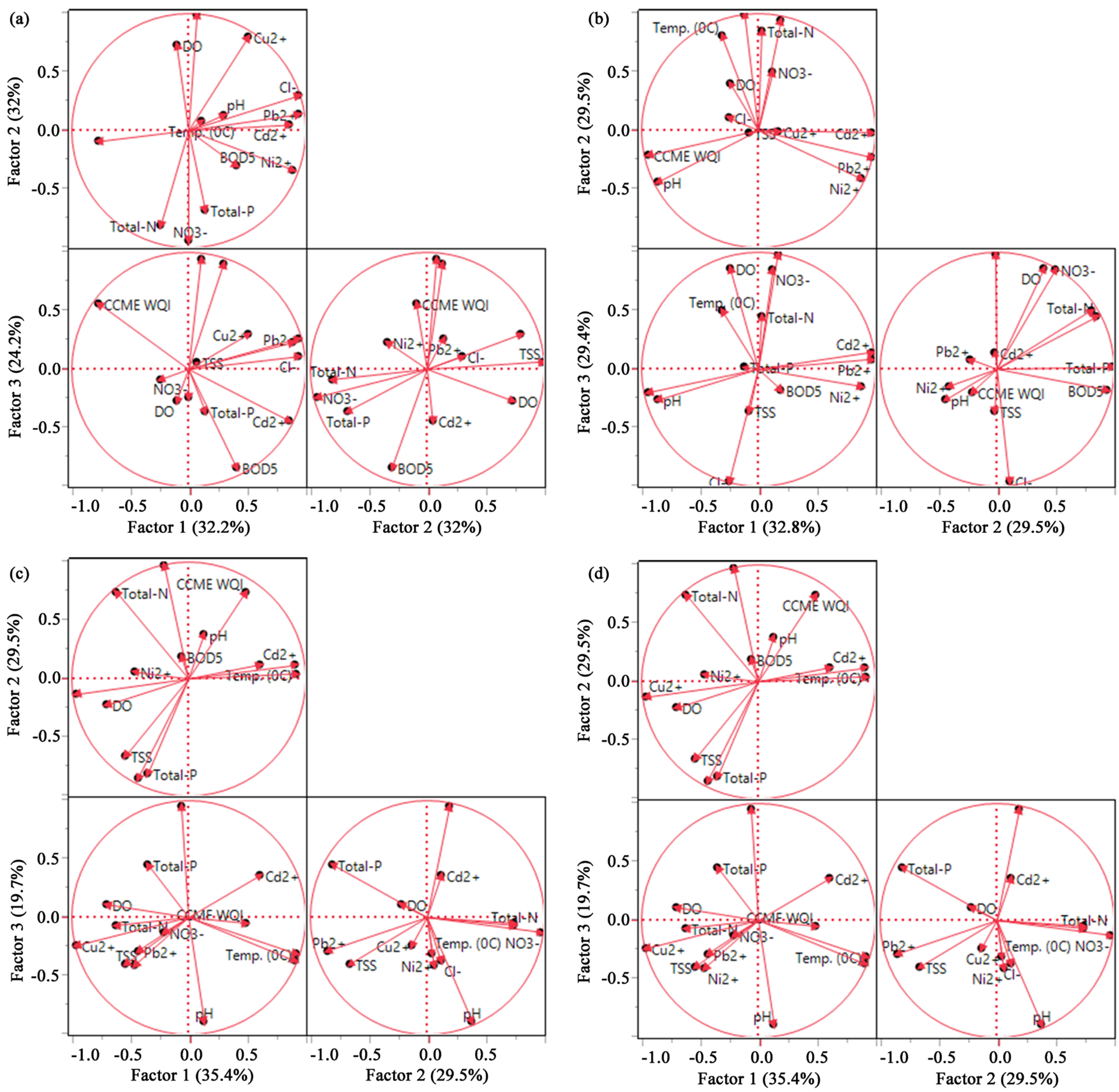

Figure 5. PCA (with Varimax rotation) of the WQI and of the physicochemical parameters as 13 variables that influence or not CCME WQI in the (a) spring, (b) summer, (c) autumn, and (d) winter seasons of 2014 to 2018, correlation F2 - F1, F2 - F3 and F3 - F1.

Total-N, while the other parameters have weaker links with the group of parameters compared above. This is also concurred by the low value (about 40%) of the variability of factors with each other.

5. Conclusion

The WQI in Seman River water was found with greater variations between seasons compared to the value trend by years, while the differences between monitoring stations were significantly higher at downstream stations compared to upper stream ones. The average values for all stations varied between 55 and 86%, classifying the water quality mainly in the class (65% - 79%). However, the average values of the downstream stations point to a significant deterioration of the water, based on the values of TSS (Total Suspended Solids), BOD_5 (Biological Oxygen Demand), DO (Dissolved Oxygen) and EC (Electrical Conductivity), parameters that are mainly related to anthropogenic factors. The multivariable Claster analysis confirms that the values of TSS, BOD_5, EC, and DO, for the entire study period are included in the first groups and are related to other interdependent groups such as pH and macronutrient contents, but with weak bonds with heavy metals and Cl^-. Based on the relations between the groups, it results that the presence of sediments, depending on the temperature and pH, condition almost all other water parameters. PCA analysis determines whether the groups of factors correlate strongly or not depending on the internal structures of the groups and variables "heavy" or latent, and vary from season to season with differentiated contributions to the water quality. All three factors influence WQI to the extent of 56% in the summer and spring season and 64% and 40% in the autumn and winter season, respectively. For better monitoring of river waters quality in Albania, more variables would have to be measured in order to prioritize the variables that affect with greater "weight", according to their origin, chemical specifications and hazards.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Abbreviation

BOD_5—Biological Oxygen Demanded
CCME—Canadian Council of Ministers of the Environment
Cd^{2+}—Cadmium ion
Cl^-—Chloride anion
Cu^{2+}—Copper ion
DO—Dissolved Oxygen
EC—Electrical Conductivity
EEC—European Economic Community
EU—European Union
F1—Factor in than means Scope in PCA—Principal Component Analysis
F2—Factor in than means Frequency in PCA—Principal Component Analysis
F3—Factor in than means Amplitude in PCA—Principal Component Analysis
ISO—International Organization for Standardization
Max—Maximum value
Min—Minimum value
NH_4^+—Ammonium cation
Ni^{2+}—Nickel ion
NO_3^-—Nitrate
Pb^{2+}—Lead ion
PCA—Principal Component Analysis
pH—potential of Hydrogen
PO_4^{3-}—Phosphate
SERR—Standard error
STDEV.s—Standard deviation
Temp. ˚C—Temperature in Celsius Degree
Total-N—Total Nitrogen
Total-P—Total Phosphorus
TSS—Total Suspended Solids
WHO—World Health Organization
WQI—Water Quality Index
$\overline{X}$—Sample Mean