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Evaluation of some streamwater quality parameters using with Principal Component Analysis (PCA) in mature *Pinus sylvestris* L. forest ecosystems

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Abstract

Aim of study: The main purpose of this study is composed to determinations of indicator water quality parameters of Oltu stream.

Area of study: The research area has been conducted in 3 different sample points on Oltu stream which is on the borders of Oltu town in the city Erzurum.

Material and Methods: The data set used in the study is composed of some selected streamwater quality parameters. In the 5 year period between 2003 and 2008, Pearson correlation analysis, Principal Component Analysis (PCA) have been applied to the dataset which was composed of the monthly result of the measurement.

Main results: 1st principal component explains of 52% of the total variance and is highly participated by Q, Ca2+, Mg2+, EC, Na+, Cl-, SO42-, SAR and B and can be thus determined as a mineral component of the streamwater. On the other principle component, it was seen that there were no correlated parameters

Research highlights: Seasonal effect was determined by sampling period can clearly be seen on the result. The research streamwater was characterized a high seasonality and it was showed dilution process of dissolved bedrock increase with winter and fall months.

Keywords: Principal Component Analysis (PCA), Water Quality Parameters, Oltu stream

Yaşlı *Pinus sylvestris* L. orman ekosistemlerinde Temel Bileşenler Analizi kullanılarak bazı akarsu kalite parametrelerinin değerlendirilmesi

Özet

Çalışmanın amacı: Bu çalışmanın ana amacı Oltu çayının indicator su kalitesi parametrelerini belirlemektir.

Çalışma alanı: Bu çalışma Erzurum ili sınırları içerisindeki Çoruh Nehrinin bir yan kolu olan Oltu Çayının üzerinde alınan 3 farklı deneme istasyonunda gerçekleştirilmiştir.

Materyal ve Yöntem: Araştırmada seçilmiş bazı akarsu su kalite parametreleri değerlendirilmiştir. 2003 ve 2008 yılları arasındaki 5 yıllık periyotta aylık değerlendirilen veri setine Pearson korelasyon analizi ve Temel Bileşenler Analizi (PCA) uygulanmıştır.

Sonuçlar Toplam varyansın %52'sini açıklayan 1. Temel bileşen özellikle Q, Ca^{2+}, Mg^{2+}, EC, Na^{+}, Cl, SO_4^{2-}, SAR ve B ile ilişkili bulunmuş ve bunlar akarsuyun mineral komponentleri olarak değerlendirilmiştir. Diğer temel bileşende ise ilişkili parameter bulunamamıştır.

Araştırma vurguları: Sonuçlar üzerinde sezonsal etkinin var olduğu açık biçimde görülebilmektedir. Araştırmada değerlendirilen akarsu yüksek sezonsallık etkisi altındadır ve çözünmüş anakayanın seyreltme (sulandırma) etkisi kış ve sonbahar mevsimlerine ait aylar ile birlikte artmaktadır.

Anahtar kelimeler: Temel Bileşenler Analizi (PCA), Su Kalitesi Parametreleri, Oltu çayı

Introduction

The stream ecosystem and its environments are most closely related hydro chemical water quality parameters in the stream (Villa and McLeod, 2002; Lake, 2007). The water quality features of a stream are represented the physical, chemical, and biological features of the watershed (Bunn et al., 1999; Fohrer et al., 2001; Leon et al., 2001; Aydın 2009). Instead of checking on all the water quality parameters in order to determine what kind of water quality features of watershed, it is indicated that focusing on some parameters are more convenient in terms of time and labor saving. The operation, which parameters response better on stream water quality analysis, is called determination of indicator parameter operation (Bayram et al., 2013; Sáncheza et al., 2007). There are a number of studies conducted on different streams about determination the indicator physicochemical parameters (Al Bakri and Kittaneh, 1998; Hall et al., 2007; Howard et al., 2004; Mogollon et al., 1993; Richter et al., 1996). By determined these indicators, not only we can have an idea of the water which is influenced by the geologic and biotic features of the watershed, but also it may provide an insight about the watershed from other regions which have the same structure (King et al., 2008; Lewis et al., 2012). Moreover, correct use of the water in accordance with understanding the quality features of the water in drinking, subsoil, industrial areas of utilization may be provided (Carr and Neary, 2008; Levick et al., 2008). For instance, in highly saline soiled areas, there will be no or limited use for irrigation purposes. Here, in this case, thanks to knowing which indicator parameter(s) are dominant, it may play a more active role in identifying the utilization purposes of the water in this region, and selecting the parameter in which the focus will help solve some negative situations in case of utilization. For example, in order to remove the negative influences of high pH of the agricultural lands which are irrigated by water and characterized with high pH, the problem is being solved by reinforcing lime to the area. Some quality parameters of water, in addition to playing a key role on deciding the water utilization purpose, they are also determinative on the health of surface water ecosystem (Norris and Thoms, 1999).

Water quality of streams is mostly influenced by anthropogenic activities other than the physicochemical feature of the rain water which is affected by geologic and biotic conditions of the watershed (Lenat and Crawford, 1994). When water quality is measured from natural or nature-like watersheds where there is no or rare anthropogenic activity, the results are generally influenced either by geological structure and vegetation or their effects. For instance, the pH values of the water in river watersheds, which is composed of coniferous trees, are high because those trees' resin, tannin, etc. substances are washed or dissolved into the water. In the subject of this study, the watershed of Oltu stream, especially in the tributaries of the stream are included mature *Pinus sylvestris* L. stands. It has been observed that the land where *Pinus sylvestris* L. trees are located, the pH is much higher compared to other parts (Bergkvist and Folkeson, 1995). Accordingly, the soil acidity is observed to increase. In a study conducted in the same way, even though *Pinus sylvestris* L. stands increase the nitrogen portion of the soil, it is seen to have a diminishing influence on phosphorous (P), potassium (P), and calcium (Ca) concentrations (Prietzel et al., 2008). Oltu watershed has alkaline bedrock which is easily dissolved and is composed of limey groundling sandy and pebbly soil (Atalay, 1982). In this kind of soils, the rain water is easily mixed with subsurface water as infiltrate and feed the river or the stream. Accordingly, the stream's qualitative features are influenced by the physicochemical features of the vegetation and the soil because of dilution effect (Bis et al., 2000).

In order to identify the physicochemical features of Oltu stream which is the subject of the study, some research has been done in the past (Yıldırım, A., 1997; Yıldırım et al. 1999). However, none of these studies are done for the purpose of finding the physicochemical indicator parameter or parameters of the water.

Material and Method

Study Area

The research area has been conducted in 3 different sample points on Oltu stream which is on the borders of Oltu town in the city Erzurum (Figure 1). The sample points are operated by State Hydraulic Works. The subject data set of the study is composed of monthly data and this data set contains 2003-2008 years. The area of Oltu watershed is 3605.3 km2. Dominating tree species in the region is Pinus sylvestris L. for many years, the semi-precious mineral known as Oltu Stone, which is formed by fossilization of Pinus sylvestris L. and other tree species, has been one of the sources of living. The regional soils are intrazonal soils with C horizon in which parent material easily dissolves and there cannot generally be covered to surface by soil (Atalay, 1982). The very alkaline soil material has appeared to the soil surface because of the erosion which is created by deterioration of the mature Pinus sylvestris L. in some parts of the forest and the area has high slope (Atalay et al.,1985).

While the upper zones of the watershed have harsh continental climate of East Anatolian Region's, the lower zones have warmer climate. According to Oltu meteorological station 1950-2005 records, average annual precipitation is 385.0 mm and average annual temperature is 9.8 ^{0}C.

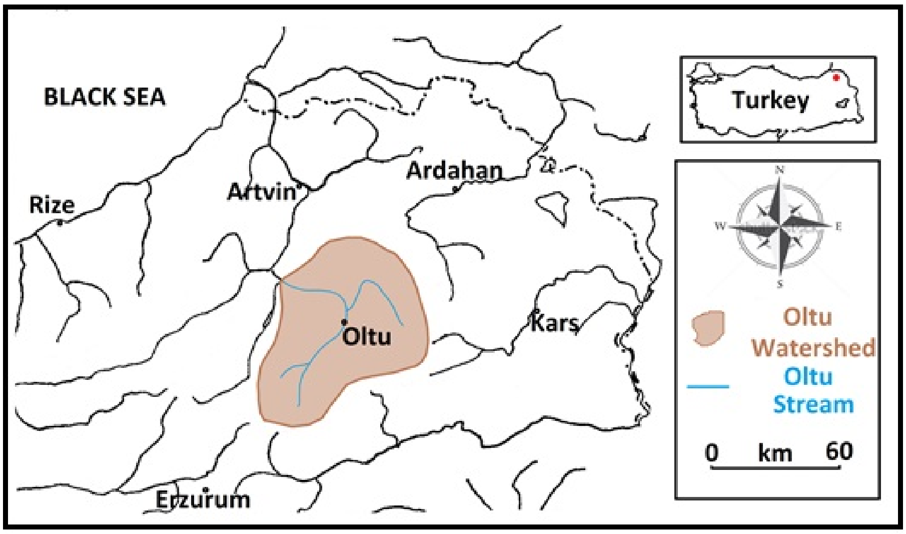

Figure 1. Location of Oltu Watershed

Method

PCA, is a multi-variable statistics technique, explains the structure of the variables on correlation or covariance matrix and it eases the explainable conditions of the relations among the variables on basis of dimension reduction (Wold et al., 1987). Thus, PCA explains a variable in the data set as new independent variables, which has a linear component and in order to find the linear components of the variable, it uses the eigenvalue of covariance matrix (Wold et al., 1987).

PCA are explained the variance as principal component. Principal components can also be determined to link between measured valuables. PCA can be expressed as the linear model;

$$Z_{ij} = \sum_{l=1}^{m} b_{jl} PC_{il}$$

Where Z is measured data; b loading coefficients of correlation between measured variables and principal components; PC is shown the score relationship between samples and principal components; i is index of samples derived from location and time of sampling; j is an index of m variables and l is an index of m principal components.

Measured water quality variables were Box-Cox transformed because PCA is known to be well perform that variables show normal distribution. Eigenvalues and eigenvectors were calculated based on the covariance matrix and the number of eigenvectors to be selected was chosen considering Kaiser's rule (Kaiser, 1960). Kaiser's rule explains that eigenvectors have with an eigenvalues greater than 1.

The data set used in the study is composed of runoff (Q), water temperature (WT), pH, electric conductivity (EC), sodium (Na^+), potassium (K^+), calcium(Ca^{2+}) and magnesium (Mg^{2+}), carbonate (CO_3^{2-}), bicarbonate(HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), sodium absorption factor (SAR), and boron (B) concentration.

Results

The twelve streamwater quality parameters and runoff were used to evaluate the average monthly values of three different station and standard deviations in Oltu stream (Table 1).

The Table 1 was shown that the large differences were not generally showed during the twelve months, although the averages of WT and EC have a big difference according the monthly average values. The average runoff values have increased in the March and April, although the concentrations of chemical parameters have decreased in these months.

The decreases of chemical parameters may be exhibited dilution effect in streamwater. The maximum dilution effect was shown in sodium concentration. Increasing the flow especially in the months of March and April was shown to effect of snowmelt-dominated stream. Despite large differences in runoff regimes in monthly trends, pH had not affected this runoff behavior.

Table 1. Average monthly values and standard deviations of some physicochemical parameters and runoff in the 5 year period between 2003 and 2008 in Oltu stream

Months	Q (m^3/sn)	WT (°C)	pH	EC (uS/cm)	Na^+ (meq/l)	K^+ (meq/l)	Ca^{2+}+ Mg^{2+} (meq/l)	CO_3^{2-} (meq/l)	HCO_3^- (meq/l)	Cl^- (meq/l)	SO_4^{2-} (meq/l)	SAR	B (mg/l)
Jan	9.01 ±4.79	2.50 ±2.18	8.46 ±0.22	805.58 ±115.64	3.22 ±1.45	0.03 ±0.02	4.86 ±0.68	0.44 ±0.23	3.60 ±0.76	1.67 ±0.52	2.40 ±1.21	2.08 ±0.93	0.82 ±0.22
Feb	11.25 ±9.29	3.75 ±2.65	8.51 ±0.10	751.83 ±158.55	3.09 ±1.53	0.03 ±0.02	4.36 ±0.64	0.42 ±0.12	3.12 ±0.53	1.61 ±0.59	2.34 ±1.26	2.05 ±0.93	0.80 ±0.27
Mar	25.76 ±33.26	6.58 ±2.75	8.45 ±0.17	680.33 ±186.85	2.47 ±1.29	0.03 ±0.02	4.28 ±0.96	0.40 ±0.19	3.15 ±0.89	1.31 ±0.63	1.91 ±0.99	1.67 ±0.78	0.63 ±0.27
Apr	66.68 ±50.69	7.58 ±1.61	8.35 ±0.18	427.42 ±153.01	1.10 ±0.58	0.02 ±0.02	3.13 ±0.97	0.27 ±0.14	2.47 ±0.80	0.56 ±0.31	0.95 ±0.99	0.86 ±0.38	0.35 ±0.26
May	67.23 ±43.52	11.75 ±2.98	8.28 ±0.14	395.08 ±85.68	1.24 ±0.63	0.01 ±0.01	2.85 ±0.51	0.29 ±0.17	2.37 ±0.39	0.57 ±0.25	0.87 ±0.47	1.02 ±0.49	0.27 ±0.18
Jun	23.11 ±18.11	13.17 ±3.72	8.34 ±0.12	627.08 ±246.55	2.78 ±2.04	0.01 ±0.01	3.90 ±1.08	0.40 ±0.19	2.93 ±0.86	1.30 ±0.86	2.08 ±1.64	1.90 ±1.16	0.50 ±0.39
Jul	11.42± 10.48	18.08 ±4.33	8.38 ±0.12	778.42 ±279.46	3.71 ±2.16	0.03 ±0.02	4.69 ±1.21	0.42 ±0.14	3.35 ±0.91	1.53 ±0.82	3.12 ±1.77	2.30 ±1.12	0.81 ±0.46
Aug	8.61 ±6.53	17.67 ±3.73	8.38 ±0.15	788.10 ±323.95	3.78 ±1.72	0.04 ±0.03	5.49 ±2.16	0.48 ±0.28	3.20 ±0.70	1.66 ±0.66	3.98 ±2.29	2.36 ±1.06	0.87 ±0.33
Sep	10.15 ±5.96	14.83 ±4.10	8.31 ±0.15	694.09 ±335.91	3.94 ±1.43	0.04 ±0.02	5.15 ±0.78	0.44 ±0.11	3.72 ±0.83	1.85 ±0.56	3.12 ±1.19	2.45 ±0.86	0.96 ±0.25
Oct	10.90 ±7.08	10.92 ±3.04	8.33 ±0.11	824.42 ±155.54	3.58 ±1.44	0.04 ±0.03	4.95 ±0.87	0.39 ±0.13	3.66 ±0.66	1.71 ±0.52	2.82 ±1.30	2.25 ±0.79	0.86 ±0.22
Now	12.97 ±7.69	5.83 ±2.94	8.31 ±0.11	767.33 ±154.46	2.82 ±1.17	0.05 ±0.03	4.84 ±1.00	0.42 ±0.14	3.51 ±0.92	1.45 ±0.42	2.34 ±1.33	1.82 ±0.73	0.74 ±0.24
Dec	10.83 ±6.88	3.75 ±1.69	8.28 ±0.15	836.58 ±126.98	3.13 ±1.33	0.04 ±0.02	5.39 ±0.63	0.39 ±0.18	4.11 ±0.63	1.64 ±0.50	2.42 ±1.14	1.89 ±0.78	0.82 ±0.28

The correlation matrix of variables was produced by Pearson Correlation Analysis in PCA (Table 2). The correlation coefficients were calculated by among the water quality parameters that affected by temporal variations. In addition to this, the coefficient should be explained the relationship statistically significant and negative correlations can be calculated between pH, Ca^{2+}, Mg^{2+}, EC, Na^{+}, K^{+},HCO_3, Cl^{-}, SO_4^{2-}, SAR and B (r = 0.55 to 0.82).

Table 2. Correlation matrix of the 13 physico-chemical variables

	Q	°C	pH	EC	Na^+	K^+	$Ca^{2+}+Mg^{2+}$	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	SAR	B
Q	1												
°C	-0.15												
pH	-0.18	-0.23											
EC	**-0.79**	0.06	0.23										
Na^+	**-0.77**	0.43	0.05	0.85									
K^+	**-0.55**	**0.17**	0.24	**0.62**	0.67								
$Ca^{2+}+Mg^{2+}$	**-0.76**	0.21	0.28	**0.87**	**0.76**	0.56							
CO_3^-	**-0.65**	0.24	0.26	**0.53**	**0.7**	0.54	0.36						
HCO_3^-	**-0.68**	-0.31	0.33	**0.81**	**0.67**	**0.44**	0.9	-0.09					
Cl^-	**-0.82**	0.24	0.17	**0.89**	**0.94**	**0.66**	**0.84**	**0.68**	0.77				
SO_4^{2-}	**-0.7**	**0.52**	-0.14	**0.79**	**0.92**	**0.65**	**0.82**	**0.56**	**0.52**	0.83			
SAR	**-0.75**	**0.44**	-0.11	**0.8**	**0.99**	**0.68**	**0.65**	**0.73**	**0.55**	**0.91**	0.89		
B	**-0.82**	0.28	0	**0.89**	**0.93**	**0.65**	**0.84**	**0.69**	**0.75**	**0.96**	**0.86**	0.9	1

In bold, significant values (except diagonal) at the level of significance alpha=0,050 (two-tailed test)

The eigenvalue scree plot (Figure 2) was used to determine the number of principal components to be specified in order to understand the basis of structure or level of their unit. The change of slope is shown that shows the number of principal component that need to be taken into consideration. Catell and Jaspars (1967) suggested considering one more principal component after the brake to slope of scree plot.

As seen from the Figure 2, brake to slope of scree plot was found after the 1st principal component. But 2, principal components were considered in this analysis by rule of Catell and Jaspars (1967). According to the Bartlett's sphericity test, observed chi-square value was found 4271.49 (critical chi-square value is 99.6). p values is lower than 0.001 (Table 3). Thus, Bartlett's test results indicate that correlation matrix was used to confirm and PCA was applicable to this data set.

Primarily, the interaction was showed up between the multiple variable statistics analysis method (PCA) and the variables. Because in PCA, 13 variables were taken into consideration for the analysis, 13 hidden principle components were created.

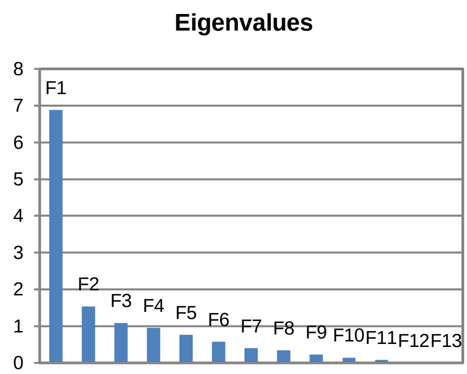

Figure 3. The eigenvalue scree plot for determine the number of PCs in the analysis

Table 3. Results of Bartlett's sphericity test

Chi-square (observed value)	4271.494
Chi-square (critical value)	99.617
DF	78
One-tailed p-value	< 0.0001
Alpha	0.05

Lower numbers of principle components which could explain the variance with a high percent were included into the evaluation. On selection of the principle component numbers were utilized to eigenvalues and the principle components whose eigenvalue was higher than 1 were included in the scope. Thus, the eigenvalue was used as criteria in deciding the number of the components in the study. 2 principle components, whose eigenvalue were higher than 1, were obtained and those explained 64.8% of the total variance on water quality data (Table 4). Only the first component explained approximately 53% of the variance. However, eigenvalues of four components was higher than 1, 1st components were focused basically (Table 4). In this table, the factor loading for principal component was presented and the bold numbers were the statistically significant values according to Malinowski significance test.

Table 4. Factor loading for principal component with eigenvalues > 1

Variable	PC1	PC2	PC3	PC4
Q	**-0.740**	-0.081	-0.120	0.125
°C	0.123	-0.484	-0.553	0.563
pH	0.043	0.220	0.613	0.741
EC	**0.859**	0.264	-0.044	-0.023
Na^+	**0.933**	-0.223	-0.028	0.004
K^+	0.519	-0.169	0.234	0.031
$Ca^{2+}+Mg^{2+}$	**0.783**	0.465	-0.199	0.114
CO_3^{2-}	0.489	-0.488	0.483	-0.156
HCO^-	0.617	0.679	-0.117	0.038
Cl^-	**0.945**	0.024	0.036	-0.067
SO^{2-}	**0.820**	-0.232	-0.215	0.139
SAR	**0.870**	-0.365	0.031	-0.029
B	**0.940**	0.001	0.003	-0.075
Exp. Var.	52.926	11.842	8.372	7.323
Cum. Exp. Var.	52.926	**64.767**	73.139	80.463

1st principal component explains of 52% of the total variance and is highly participated by Q, Ca^{2+}, Mg^{2+}, EC, Na^+, Cl^-, SO_4^{2-}, SAR and B and can be thus determined as a mineral component of the streamwater. This component (PC1) is likely from dissolution of bedrock structure. It was observed that there was a negative relation between the runoff and this mineral component. The representation of the parameter values on the two dimensional surface by the first two factors is shown on Figure 3. We interpreted this principal component as "salinity group".

As seen from the Figure 3, the parameters which are high connected to the runoff are situated closer to the horizontal axis. The highest negative relation was seen between the runoff and chloride. On the other principle components, it was seen that there were no related parameters.

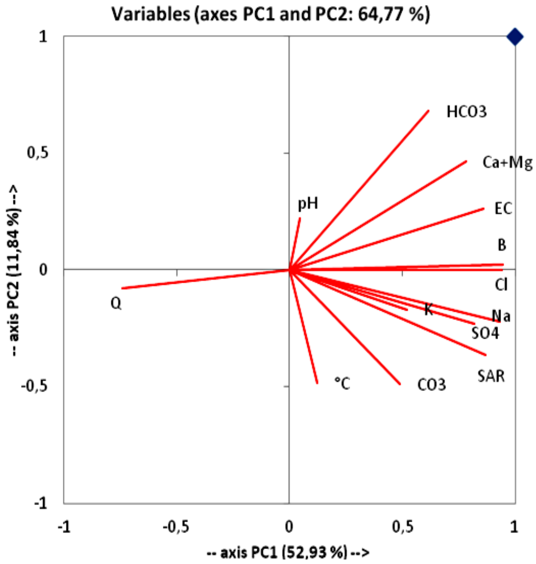

Figure 3. Ordination diagram of PCA of water quality parameters and runoff

Sampling time displays with factor scores of sample on the biplot defined by wet and dry periods of years (Figure 4). Positive or negative scores of axis PC1 on the biplot indicate high seasonality, whereas sampling months with negative and positive factor scores on PC1 axis will correspond to runoff and salinity component of streamwater. Runoff has a negative factor scores and salinity components have positive factor scores on biplot (Figure 4). As pointed above, some months of the years especially July of 2006 was highly dry period and that fact is displayed by high factor scores of salinity component.

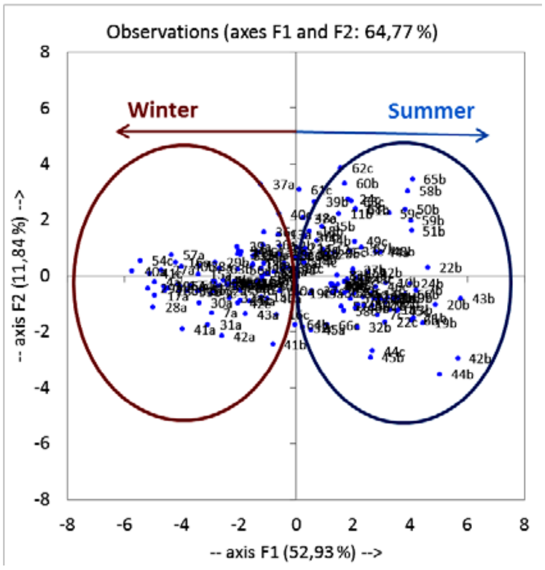

Figure 4. Seasonal effect on the biplot

Seasonal effect was determined by sampling period can clearly be seen on the biplot (Figure4). Therefore interaction between sampling time and dilution affect has been simultaneously constructed salinity components derived from dissolved bedrock and runoff. The research streamwater was characterized a high seasonality and it was showed dilution process of dissolved bedrock increase with winter and fall months.

Discussion

The parameter connection on principle components helps to find how these waters are characterized or in other words, it helps the indicator feature to be found. After determining these indicator parameters with PCA the parameters were determined to water quality for Oltu stream. PCA provides the understanding that the salinity feature has the dominant character in these waters. Sodium, chloride, electric conductivity and sodium absorption ratio parameters having higher related coefficient of determination than the other parameters explains the situation. So, the salinity was the indicator feature of Oltu stream. This situation is considered to derived from the bedrock features. With no such intensive soil which may have an influence on the water quality features of the decomposition material in the watershed. Decomposition was not at a good level because of the low humidity conditions. In the meantime, a negative relation has been found between this indicator feature (salinity) and the runoff. It has been proved that during spring when the runoff increases the salinity concentration decreases and during summer period salinity increases in the water. Runoff contributes negatively to this dominant salinity factor (first principal component), which can be explain dilution effect of dissolved minerals increase with runoff. Vega et al. (1998) also show dilution effect in their research. One of the most important results of this study that the runoff was able to change water quality and especially the salinity features of these waters. Similarly, Na^+, Cl^-, EC, SAR, SO_4^{2-} and B parameters were also determined the indicator parameters of Oltu stream. The physicochemical characterization of Oltu stream might be strongly influenced by the soil-water interaction. Besides, the dilution effect was shown in Oltu stream which has characterized snowmelt-dominated stream (Table 1). Physical parameters (EC, WT and pH) has not influenced to the dilution effect of runoff. McNeil et al. (2005) emphasized in their study that the chemistry limits of the waters might be changed the geologic condition of the region. Determining the average pH value of Oltu stream water which has calcareous soil composed of alkaline bedrock as 8.5 constitutes the simplest example of this influence. Anderson et al. (1993) revealed in their study that when an acidic characteristics stream meets with a shunt coming from a calcareous region. the water turns into alkali character. The findings similar to our study have shown that bedrock may a very important factor on hydro-chemical features of the watershed. But, it is also true that the stream turns into an acidic structure when coniferous trees, resin, tannin etc. are dominant in a region because they hold acidic matters on themselves (Wiklander et al.. 1991). However, the findings of this study were observed to be similar with the findings of Anderson et al. (1993). Oltu stream which has a slightly acidic structure because of mature *Pinus sylvestris* L. located especially on upper zones of its watershed. In fact, the stream has an alkaline structure because of its dominant geologic conditions of watershed.

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