

Application of Multivariate Statistical Analysis in Assessing Surface Water Quality of Chamera-I Reservoir on River Ravi

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Abstract: *The present investigation was carried out on Chamera - I reservoir located in Chamba district of Himachal Pradesh from January, 2010 to February, 2012 to study temporal changes in physico-chemical factors. Water quality samples were subjected to various chemometric methods like cluster analysis (CA), Principal Component analysis (PCA) and correlation (r) & regression analysis (RA) that identified and related most significant water quality parameters (WQPs). A dendrogram from the cluster analysis showed 2 major clusters separating rainy season from the other three seasons on temporal scale in the study area. PCA selected 3 variables accounting for 100% of total variance for water quality on temporal scale. The correlation coefficient r ranged from ± 0.9 to 1.0. The obtained correlation values were then subjected to regression analysis suggesting significant linear relationship between various WQPs.*

Keywords: Chamera-I reservoir, temporal variations, water quality, multivariate statistical analysis

1. Introduction

Lotic systems are the most important inland water resources for various human needs. Due to this water quality has become one of the major environmental concerns worldwide as it is influenced by natural and anthropogenic disturbances [18]. In recent years, surface water quality has become a matter of serious concern as it is directly linked with human well being. Due to this, freshwater reservoirs are also impacted by several inputs from the surroundings [11]. The reservoirs have important use in irrigation, hydroelectric generation and drinking purpose. Therefore it has become crucial to establish monitoring programs to draft suitable measures for reduction of hazardous substances in aquatic ecosystems that endangers the biota and human life [23]. For reducing the complexity of large water quality data multivariate statistical analysis of water quality parameters (WQPs) should be conducted. These chemometric methods like Correlation analysis, Regression analysis, Factor analysis/Principal Component Analysis (FA/PCA) and cluster analysis (CA) are useful for reducing the clutter of large datasets and obtain meaningful results [3], [22], [17], [12], [19], [21], [9].

In recent years, many studies related to these methods have been carried out. For instance, multivariate statistical methods, such as PCA/FA and CA were used [16] to identify the sources of water pollution of Alqueva's reservoir, Portugal. By using three multivariate techniques FA, PCA, and DA spatial and temporal changes in the Suquia River were reported in Argentina [22]. Similarly, FA, PCA and DA techniques were used [12], [13] to study the water quality and apportionment of pollution sources of Gomti river (India). Further, multivariate methods, like CA, DA and PCA/FA were used [20] to analyze the water quality dataset of

Mekong river and Fuji river basin from 1995-2002 to obtain temporal and spatial variations and to identify potential pollution sources. In 2013, [14] correlation and regression analysis was applied in assessing ground water quality and found out that EC and TDS have high correlation with most of the parameters throughout different seasons. Then they recommended treatment of tube well water for drinking purposes. Also, [6] correlation coefficient values were used to select proper treatments to minimize the contaminations of Ganga river water in Haridwar.



Figure 1: Google earth map showing Chamera I reservoir

The Chamera I reservoir ($32^{\circ}36'65''$ N $75^{\circ}59'70''$ E) is located on the Ravi river and supports the hydroelectricity project in the region formed by Chamera-I Dam. It is located near the town of Dalhousie in the Chamba district in the state of Himachal Pradesh in India. The reservoir of the dam is the Chamera Lake. The reservoir behind the dam extends to 18 km upstream of river Ravi and 11 km along the river Siul also. The surface area of the reservoir is approximately 9.5

sq. km. Ravi river has a total catchment area of 5,451 sq. km and 154 sq. km in Himachal Pradesh. This basin lies between the Pir Panjal and Dhauladhar ranges of Himalayas [10].

The present study was aimed to investigate the physico-chemical changes in water quality of Chamera I reservoir during the years 2010-2012. By using various multivariate data reduction techniques like PCA/FA, CA, RA we can determine the differences and similarities between monitoring periods and also establish the role of significant WQPs that influence the temporal variations in water quality of the reservoir.

2. Methods

Water samples for four seasons (summer, rainy, winter and spring) were collected over a 24 month period. Grab samples were collected in pre-treated and labelled plastic bottles and were immediately preserved and analyzed following standard protocols given in APHA/ AWWA/WEF [2]. All water samples were stored in insulated cooler containing cool packs at 4°C until processing and analysis. Portable water analyzer Kit (WTW Multy 340ii/ SET) was used to measure four water quality parameters on site and these were pH, water temperature (WT), dissolved oxygen (DO) and electrical conductivity (EC). Biochemical Oxygen Demand (BOD) was calculated using Oxitop measuring system for five days at 20°C in a thermostat (TS 606-G/2-i). Alkalinity (AK), Acidity (AD), Total Hardness (TH), Calcium (Ca), Magnesium (Mg), Free CO₂ (CO₂) Chlorides (Cl), Total Solids (TS), Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) were calculated using standard methods recommended in manual of APHA/AWWA/WEF (2005). Chemical Oxygen Demand (COD), Ammonia (NH₄-N), Total Phosphate (ΣP), and heavy metals - Lead (Pb), Maganese (Mn), Nickel (Ni), Chromate (Cr) and Cadmium (Cd) analysis were measured using Merck cell test kits & heavy metal testing kits on UV/VIS spectrophotometer (Spectroquant® Pharo 300).

The variables chosen for present study were normally distributed as confirmed by Kolmogorov Smirnov (Ke-S) statistics. Correlation matrix (Pearson's r) was constructed using the mean values (seasons) of studied parameters using STATISTICA Software. Significant correlated values between different parameters were further tested for linear regression. The water quality data sets, standardized through z scale transformation (23 variables) were subjected to three multivariate techniques: cluster analysis (CA), principal component analysis/ factor analysis (PCA/FA) and regression analysis (RA). All statistical tests and computations were performed using the SPSS statistical software (Version 16.00) and STATISTICA 12.

Pearson correlation (r) matrix was applied to all samples for different seasons for identifying the possible statistical relationship between different WQPs. Only values from ± 0.9 to 1 were taken from Pearson's correlation to find regression equation between different parameters with their P and F values. RA was carried out in order to know the nature and magnitude of the relationship among various physicochemical parameters.

PCA/FA was executed on the mean values of seasonal data sets (23 variables) to identify the factors influencing the water quality and to evaluate the significant differences among the sampling seasons [20]. PCA/FA technique was used to transform the original and interrelated water quality variables into uncorrelated and fewer variables called Principal Components (PCs) for extracting the useful information [22],[20]. After that less significant PCs (eigenvalues less than 1) were eliminated through varimax rotation of the axis defined by PCA. For better interpretation of results a new group of variables were obtained known as Varifactors (VFs). Varifactor loadings were classified as >0.75, 0.75-0.50 0.50-0.30 respectively as strong, moderate and weak [5].

Cluster analysis was applied to the water quality data sets obtained for two year period in order to group the similar sampling seasons (temporal variability). In this study, Hierarchical agglomerative CA on normalized seasonal mean data using Bray Curtis (similarity or dissimilarity) and Ward's method (distance) with squared Euclidean distances was performed. A dendrogram was generated that showed clustering processes on basis of proximity of objects [22], [17], [12], [13], [20].

3. Results

Table 1: Water quality characteristics of Chamera-I reservoir

Variable	Mean± S.E.	Limit	PL (BIS*)	(MPL)
WT	7.97±1.95	3.90 - 13.25	-	-
pH	8.00 ±0.94	6.47 - 10.67	6.5-8.5	-
BOD	18.29±5.64	5.17 -32.33	-	-
DO	9.31±2.51	4.40 - 13.74	-	-
COD	17.53±14.16	0.93 - 59.67	-	-
EC	181.83±9.71	160.83 - 03.17	-	-
TS	215.42±25.74	171.67-290.00	-	-
TDS	91.67±20.92	45.00 - 140.00	500	2000
TSS	122.50±17.62	85.00 - 155.00	-	-
CO ₂	20.53±3.82	9.53 - 26.40	-	-
AK	50.42±13.32	20.00 - 85.00	200	600
AD	25.83±6.68	10.83 -43.33	-	-
Cl	20.83±5.87	8.99 - 36.92	250	1000
TH	49.00±15.17	26.00 - 93.67	300	600
Ca	10.49±3.01	6.41 - 19.24	75	200
Mg	5.57±2.00	2.27 - 11.13	30	-
Ni	0.16±0.08	0.02 - 0.37	-	-
NH ₄	0.19±0.19	0.00 - 0.75	-	-
Pb	0.24±0.12	0.10 - 0.60	0.05	-
Cd	0.16±0.05	0.06 - 0.28	0.01	-
Cr	0.13±0.03	0.07 - 0.22	-	-
Mn	0.39±0.13	0.05 - 0.63	0.1	0.3
ΣP	0.23±0.17	0.03 - 0.75	-	-

Note: BIS (Bureau of Indian Standards); PL- Permissible Limit; MPL-Maximum Permissible Limit; All parameters were measured in mg/l except WT-°C; pH- pH; EC- μS/cm;

Table 1 represents summary of mean ± S.E. values, limits and range of 23 physicochemical WQPs of Chamera I reservoir studied for four seasons (summer, winter, spring and rainy) over a period of two years. The average concentration of heavy metals like Pb, Cd and Mn were higher than the recommended permissible limits of drinking water stated under Bureau of Indian Standards [4]. This is due to leaching

of natural deposits and withering of rocks from surrounding hills. All these parameters showed significant temporal variation in different months. WT showed a range of 9.35 which results in growth of aquatic organisms. pH value is alkaline for rainy season. The value of BOD and COD is highest for summer season suggesting the greater influx of domestic sewage during dry months of low flow. Similarly the values of suspended solids were well within permissible limits but the values of TS, TDS and TSS were higher during rainy season suggesting nutrient loading due to natural and anthropogenic activities. Likewise, the values of TH, Ca and Mg were also high during rainy season as compared to other three seasons.

Cluster Analysis

A dendrogram was constructed to identify temporal similarity or dissimilarities (Bray Curtis) and distance (Ward’s method) between different sampling seasons using cluster analysis. Cluster analysis grouped 4 seasons into 2 clusters: cluster I corresponds to rainy season and cluster II grouped the rest of the three seasons (spring, summer and winter) together. The cophenetic correlation was 0.9809 for Ward’s Euclidean distance. Rainy season was the most dissimilar season in terms of distance between both clusters was 235.67. Winter and spring seasons showed nearest distance of 78.8 followed by summer and winter with the value of 87.4 (Fig. 2A). The results obtained through Ward’s method were further supported by Bray Curtis method of clustering. The cophenetic correlation was 0.9538 for Bray Curtis. The least similarity was seen between rainy and other 3 seasons separating them into two clusters. The percentage of similarity between winter and spring was highest (84.4%) followed by winter and summer (83.1%) (Fig. 2B). These two dendrograms confirmed our finding that water quality of rainy season was different from other three seasons under study in terms of similarity and distance indices.

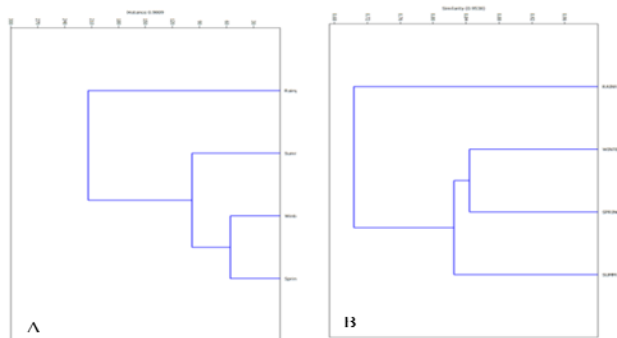


Figure 2: Dendrogram showing temporal clustering (A- Euclidean Distance; B- Bray-Curtis)

Regression Analysis (RA)

Temporal variations in river water quality parameters were further evaluated through a season parameter correlation matrix, which shows that all the measured parameters (13 in number) were found to be significantly ($p < 0.05$) correlated with the season between ± 0.9 -1.00. There is no correlation between EC, TDS, TSS, CO₂, BOD, COD, NH₄-N, Cd and Mn. The season-correlated parameter can be taken as representing the major source of temporal variations in water

quality. Wide seasonal variations in temperature and river discharge can be attributed to the high seasonality in various water quality parameters. The results of correlation analysis showed Ni and TS are having high correlation with most of the parameters followed by Ca, Mg, Pb, AK, TH, AD, DO, pH, Cl, Cr and $\sum P$. The correlation coefficient and their respective F and P values are given in table 2.

Table 2: General Linear regression model among significantly correlated parameters of Chamera-I reservoir

Y	X	r	F	P value	Significant
Pb	pH	0.919	10.47	0.084	L.S.
	Ca	0.997	50.34	0.019	S.S
	Mg	0.983	8.68	0.099	L.S.
Cr	BOD	0.918	10.63	0.083	L.S.
	COD	0.955	17.06	0.054	S.S
Ni	pH	0.981	48.03	0.020	S.S
	Cl _s	0.909	8.89	0.096	L.S.
	Mg	0.915	32.51	0.029	S.S
	DO	-0.941	16.00	0.057	S.S
	TS	0.918	10.57	0.083	L.S.
	TDS	0.930	12.26	0.073	L.S.
P	AK	0.911	10.03	0.087	L.S.
	AD	0.904	9.09	0.095	L.S.
	CO ₂	-0.943	16.64	0.055	S.S
TH	TS	0.958	13.25	0.068	L.S.
	pH	0.950	19.75	0.047	S.S
	Pb	0.994	34.44	0.028	S.S
Ca	pH	0.911	5.30	0.148	N.S.
	Mn	-0.915	25.67	0.037	S.S
	Cl	0.915	8.77	0.098	L.S.
	TH	0.994	25.56	0.037	S.S.
Mg	Cl	0.951	44.45	0.022	S.S.
	TH	0.997	31.00	0.031	S.S.
	pH	0.972	58.53	0.017	S.S
AK	Ca	0.982	6.06	0.133	N.S
	WT	0.991	107.64	0.009	S.S
	pH	0.937	14.24	0.064	S.S
AD	AD	0.999	2090.01	0.000	S.S
	WT	0.995	180.37	0.005	S.S
	pH	0.935	13.84	0.065	S.S
DO	EC	-0.922	11.37	0.078	L.S.
	TDS	-0.939	14.96	0.061	L.S.
pH	WT	0.929	12.58	0.071	L.S.
	TS	0.987	35.22	0.027	S.S
Cl	pH	0.930	12.74	0.070	L.S.
	TDS	0.948	17.79	0.052	S.S
TS	WT	0.981	50.05	0.019	S.S
	AK	0.991	27.68	0.034	S.S
	AD	0.995	31.66	0.030	S.S
	Pb	0.952	18.73	0.049	S.S
	Ca	0.934	6.51	0.125	N.S.
Mg	0.968	11.72	0.076	L.S.	

Note: Y (Independent variable); X (Dependent variable); r (Karl Pearson’s correlation coefficient values significant at 0.05 level); S.S (Strong Significance); L.S. (Low Significance); N.S.(No Significance)

To determine and explain the nature of relationship between various WQPs we plotted concentrations of all dependent variables against independent variables. Concentrations of most variables increased with increasing independent variables. These parameters were then formulated for regression equations given in Figure 3(A-N).

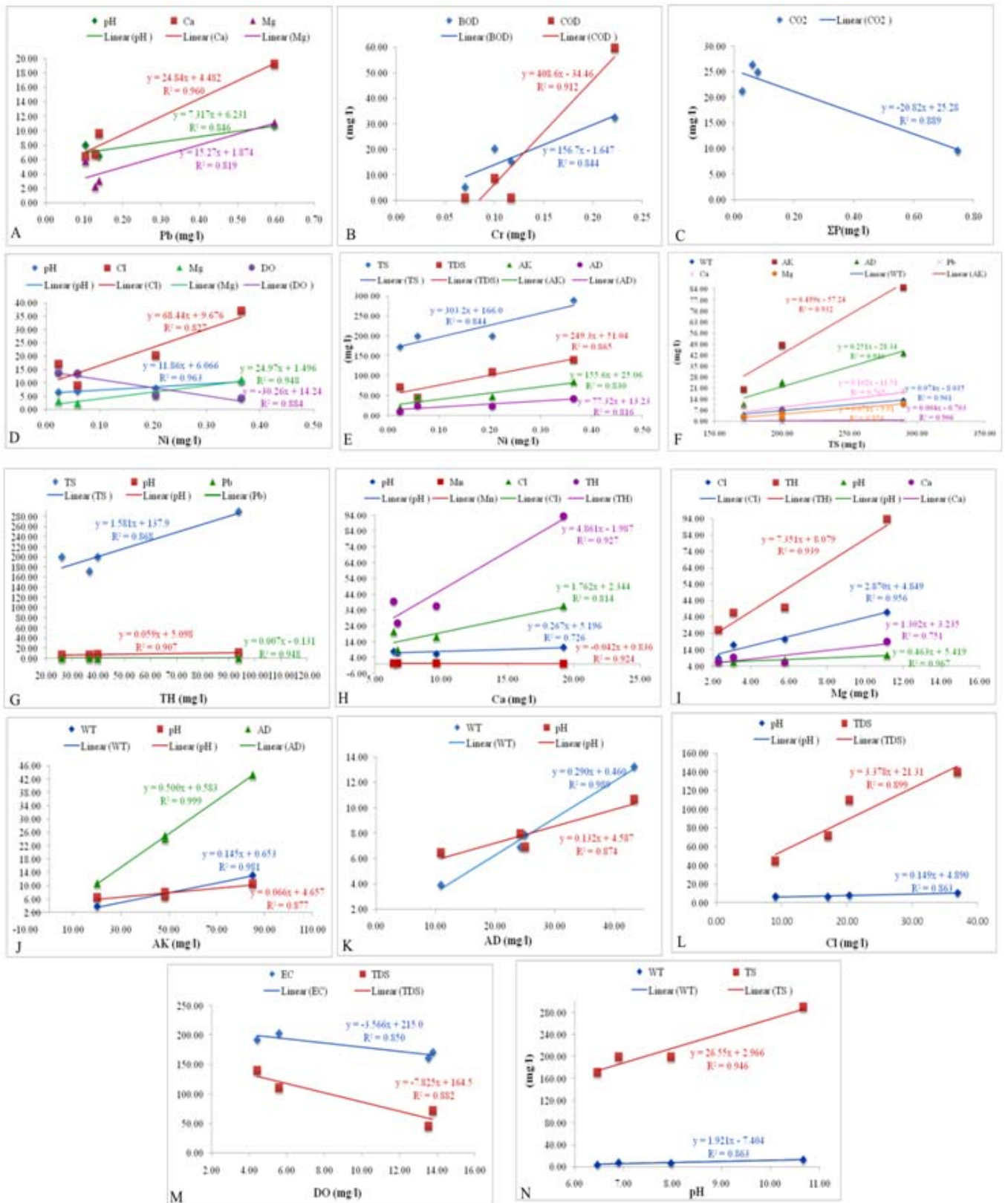


Figure 3: Plots of water quality parameters as a linear regression model (A-N)

Note: Average values of the parameters on X and Y axis were taken in mg/l except for pH and EC

Principal Component Analysis

The screen plot was used to identify the number of PCs during seasonal sampling of physicochemical parameters.

The 23 physicochemical parameters were reduced to 3 main factors i.e. factor 1, 2 and 3 (Fig. 4). A pronounced change of slope was seen after the 3rd eigenvalue as the remaining 20 factors have eigenvalues of less than one and therefore not

considered significant. Loading of three retained PCs are shown in table 4. PC1 explains 59.4% of the variance and is highly contributed by variables with highest positive factor loadings (>0.90) such as WT, pH, TS, TDS, AK, AD, Cl, TH, Ca, Mg, Ni and Pb whereas DO and Mn has strong negative loadings. High positive loadings indicated strong linear correlation between the factors and water quality parameters. PC2 explains 21.5% of the variance and includes COD, EC and Cr. PC3 explains 19.1% of variance contributed to it by CO₂, NH₄-N and Cd. These high values are indicative of high agricultural runoff and erosion from surrounding hills.

A rotation of PCs can achieve a simpler and more meaningful representation of the underlying factors by decreasing contributions to PCs by variables with minor significance and increasing the more significant ones. Although rotation does not affect the goodness of fitting of principal components solution, the variance explained by each factor is modified [9]. A varimax rotation of principal components to rotated PCs (called henceforth varifactors) is presented in (Table 4). Therefore 3 varifactors (VF) were extracted, explaining 100% of the variance in data sets. It must be noted that rotation were resulted in an increase in the number of factors necessary to explain the same amount of variance in the original data set. Therefore, the VF1 (51.4%) explained less variance than shown before rotation. Similar conclusions were explained on spatial and temporal variation in water quality of Jajrood River [9]. VF1 showed high positive scores on pH, TS, TDS, Cl, TH, Ca, Mg, Ni and Pb with DO, Cd and Mn having negative load. VF2, showed 24.4% of the total variance which showed high negative loading of BOD, COD and Cr with only TSS showing strong positive loading. The increased level of BOD and COD is due to anthropogenic interference from the surroundings [7],[20]. VF3 (24.1% of variance) has a high and positive load of CO₂ whereas only SP has strong negative load.

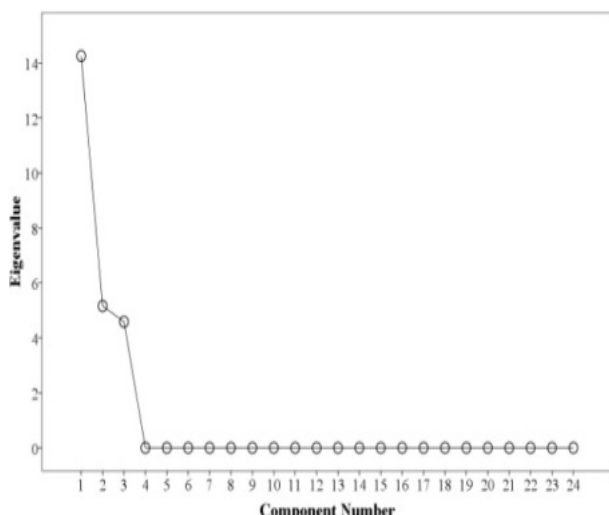


Figure 4: Scree plot of eigen values showing temporal variations

Table 4: Loadings of temporal water quality variables on principal and rotated components

	Principal Components			Rotated Components		
	PC1	PC2	PC3	VF1	VF2	VF3
WT	.942	-.015	.334	.701	.385	.600
pH	.991	.131	-.010	.911	.163	.380
BOD	-.656	.724	-.214	-.392	-.912	-.123
DO	-.786	-.605	.127	-.844	.362	-.395
COD	-.214	.954	-.208	.034	-.992	.122
EC	.515	.780	-.354	.723	-.668	.177
TS	.988	-.043	.145	.818	.368	.443
TDS	.843	.377	-.384	.971	-.216	.105
TSS	.454	-.581	.676	.038	.862	.505
CO2	.225	.514	.828	-.073	-.153	.985
AK	.932	.120	.342	.708	.262	.656
AD	.935	.089	.344	.704	.292	.647
Cl	.925	.066	-.373	.995	.094	.021
TH	.979	-.163	-.120	.904	.395	.166
Ca	.953	-.270	-.138	.872	.478	.100
Mg	.991	-.085	-.106	.919	.331	.213
Ni	.945	.326	-.020	.902	-.031	.431
NH4-N	-.370	-.314	.874	-.745	.442	.500
Pb	.960	-.272	-.069	.849	.503	.161
Cd	-.649	.080	.756	-.889	-.032	.458
Cr	-.411	.910	.051	-.258	-.930	.260
Mn	-.756	.545	.363	-.751	-.604	.266
P	-.532	-.449	-.718	-.238	.039	-.970
Eigen Value	14.26	5.16	4.58	12.35	5.86	5.79
%Total Variance	59.40	21.5	19.1	51.5	24.4	24.1
Cumulative %	59.40	80.9	100.0	51.5	75.9	100.0

4. Conclusion

The present study assessed the temporal variability and water quality using multivariate statistics in the Chamera-I reservoir in Himachal Pradesh. All sampled parameters were within permissible limits of BIS. These parameters also showed a trend in seasonal variation. The higher concentration of heavy metals like Pb, Cd and Mn in the surface water can be attributed to discharge of domestic wastes from catchment area and due to natural erosion of mineral & soil deposits from the surrounding hills. A systematic correlation and regression in this study showed that there is a significant linear relationship between different pairs of water quality parameters which can be used to determine the water quality. It can be concluded that Ni and TS are the most important WQPs as they are correlated with most of the variables. Results of regression analysis also showed that during rainy season, runoff increases the concentration of most inorganic parameters. Hierarchical cluster analysis grouped the sampling seasons into 2 seasons suggesting inorganic runoff from the surrounding hills. The results from PCA also suggested that most variations in water quality are due to natural soluble salts and domestic sewage.

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