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Assessment of Seasonal Variation in Surface Water Quality of Savitri River by Using Multivariate Statistical Techniques

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Abstract: An attempt was made to study the physico-chemical parameters of Savitri river water using multivariate statistical techniques such as principal component analysis (PCA) and hierarchical cluster analysis. In this study, data of 26 water quality parameters for six sampling locations were analyzed during monsoon, winter and summer season of June, 2004 to May, 2007. Scree plots for the eigenvalues obtained in this study shows pronounced seasonal change in slope. Water Quality Index (WQI) values were found to be increasing during the seasons and indicate the deterioration of water quality in summer season. Cluster analysis demonstrates that the surface water character changes significantly with seasons.

Key words: Principal component analysis, cluster analysis, water quality index.

Introduction

Assessment of seasonal change in surface water quality is an important aspect for evaluation of temporal variations of river pollution due to natural or anthropogenic inputs of point and non-point sources. Agricultural, industrial and urban activities are considered as being major sources of chemicals and nutrients to ecosystem (Ouyang, 2006; Khan et al., 2009). The degradation of water quality due to various contaminants has resulted in altered species composition and decreased overall health of aquatic communities within the river basin (Durell et al., 2001).

Due to spatial and temporal variations in water chemistry a monitoring programme that will provide a representative and reliable estimation of the quality of surface waters is necessary. Thus, monitoring programme including frequent water samplings at many sites and determination of a large number of physico-chemical parameters are usually conducted, resulting in a large data matrix, which needs a complex data interpretation (Chapman, 1998; Fakayode, 2005; Dwivedi and Pathak, 2009). The evaluation of water quality in developing countries has become a critical issue in recent years (Ongley, 1998), especially due to the concern that fresh water will be a scarce resource in the future whereas water monitoring for different purposes is well defined (e.g. aquatic life preservation, contact recreation, drinking water use) (Chapman, 1992; WHO, 1987).

The problems of data reduction and interpretation, characteristic change in water quality parameters and indicator parameters, and identification can be approached through the use of the principal component analysis (PCA), principal factor analysis (PFA) and cluster analysis (Ouyang et al., 2000). The multivariate analysis techniques are used to explain the correlation among a large number of variables in terms of small number of underlying factors without losing much information (Meglen, 1992). The intention underlying the use of multivariate analysis is to achieve great

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efficiency of data compression from the original data and to gain some information useful in the interpretation of the environmental geochemical origin. In recent years, the PCA and PFA techniques have been applied to a variety of environmental applications (Ouyang, 2006; Gangopadhya et al., 2001).

Water quality indices (WQI) permit us to assess changes in water quality and to identify water trends (Chapman, 1992). A quality index is a unitless number that ascribes a quality value to an aggregate set of measured parameters. The WQI gives a number that can be associated with a quality percentage, easy to understand by everyone and based on scientific criteria.

Materials and Methods

Study Area

The study area of Savitri river basin located near Mahad of Konkan region in India at 18° 05′ North and 73° 25′ East. Mahad industrial area lies on the right bank of Savitri river. It is one of the major rivers in the Konkan region. It starts at Mahableshwar, flows through the hilly area and merges into the Arabian sea which is 40 km away from the Mahad. Kalu river, Gandhari river and one water stream (which flows through the industrial area) joins the Savitri river. Sewage of Mahad city is also discharged into the river. Pharmaceutical, pesticide, dye and dye intermediate industries are located in Mahad industrial area that discharges large quantities of waste water in the river and hence pollutes the river.

Sample Collection

Samples were collected during the monsoon, winter and summer seasons of June 2004 to May 2007 from Savitri river and one canal/stream that joins Savitri river. All samples were collected in pre-cleaned HDPE sample container of 2000 ml capacity. Sample containers were completely filled with water sample to eliminate any headspace and dissolution of oxygen from air. Prior to collecting the samples, bottles were rinsed with sample water. After sample collection, the containers were labeled, wrapped with parafilm and stored on ice for transport. All samples were stored in laboratory in their original containers at 4°C.

Analysis of River Water

The physico-chemical analysis of water quality parameters were analyzed by following the Standard Methods by APHA (1992). Cation and anion analysis were carried out on Ion-Chromatograph instrument (Make-Metrohm). Eluents used for anion analysis was 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$, column used: A-SUPP-5, Flow rate: 0.7 ml/min, pressure: 10.6 Mpa and for cation column used was Metrsep C2-250, eluent: 4 mMol/L tartaric acid/0.75 mMol/L dipicolinic acid, flow rate: 1ml/min and pressure 10.1 Mpa was maintained.

Results and Discussion

Water Quality Index (WQI)

Water quality indices for major Indian rivers were reported and it was found that the WQI values were above 100 implying that the water of these rivers was not fit for human consumption without proper treatment (Tiwari and Manzoor Ali, 1998).

In the present study, WQI (Figure 1) for Savitri river reveals the information regarding the status of water pollution at all six sampling stations of study area. WQI values at all locations and during all seasons are above 100 except sampling station (IV); this indicates that river water is not fit for drinking purpose. WQI values for sampling stations I, II and III are approximately equal for monsoon season of year 2004 and summer season of year 2007 but shows variations for other seasons (Figure 1). Water quality index values for stations V and VI were

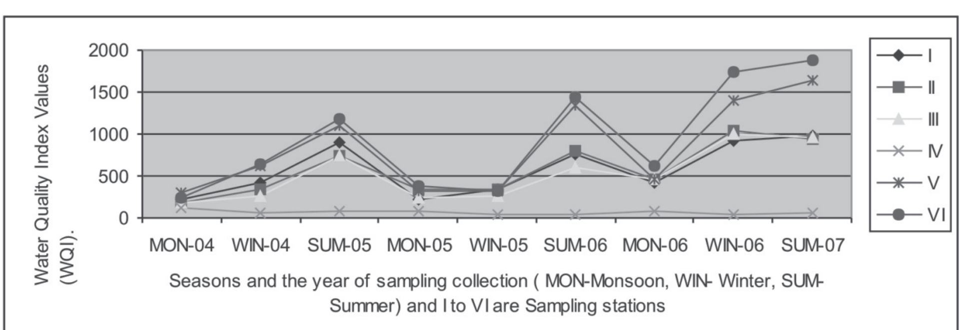

Figure 1: Seasonal variation in water quality index (WQI) of different sampling locations.

increased by 20% in summer season during the period Summer-2005 to Summer-2007. In the monsoon season, WQI values were doubled but these values are ranging 200-600. WQI values decreased in winter season of the year 2005 and again increased in winter-06. Savitri river water quality was observed deteriorated during the sampling period Jun-2004 to May-2007.

Principal Component Analysis

In PCA, eigenvalues are normally used to determine the number of principal components (PCs) retained for further study (Y. Ouyang et al., 2006). Number of components are equal to the number of variables in PCA. However the component is not only comprised of a single variable but rather all variables used in a study. For example, there were 26 variables used in this study, which produced 26 components. Principal components were extracted from the correlation matrix and with eigenvalues greater than one. Principal component score plots for PC1 and PC2 are shown in Figure 2.

Scree plot for the eigenvalues obtained in this study shows pronounced seasonal change in slope (Figure 3).

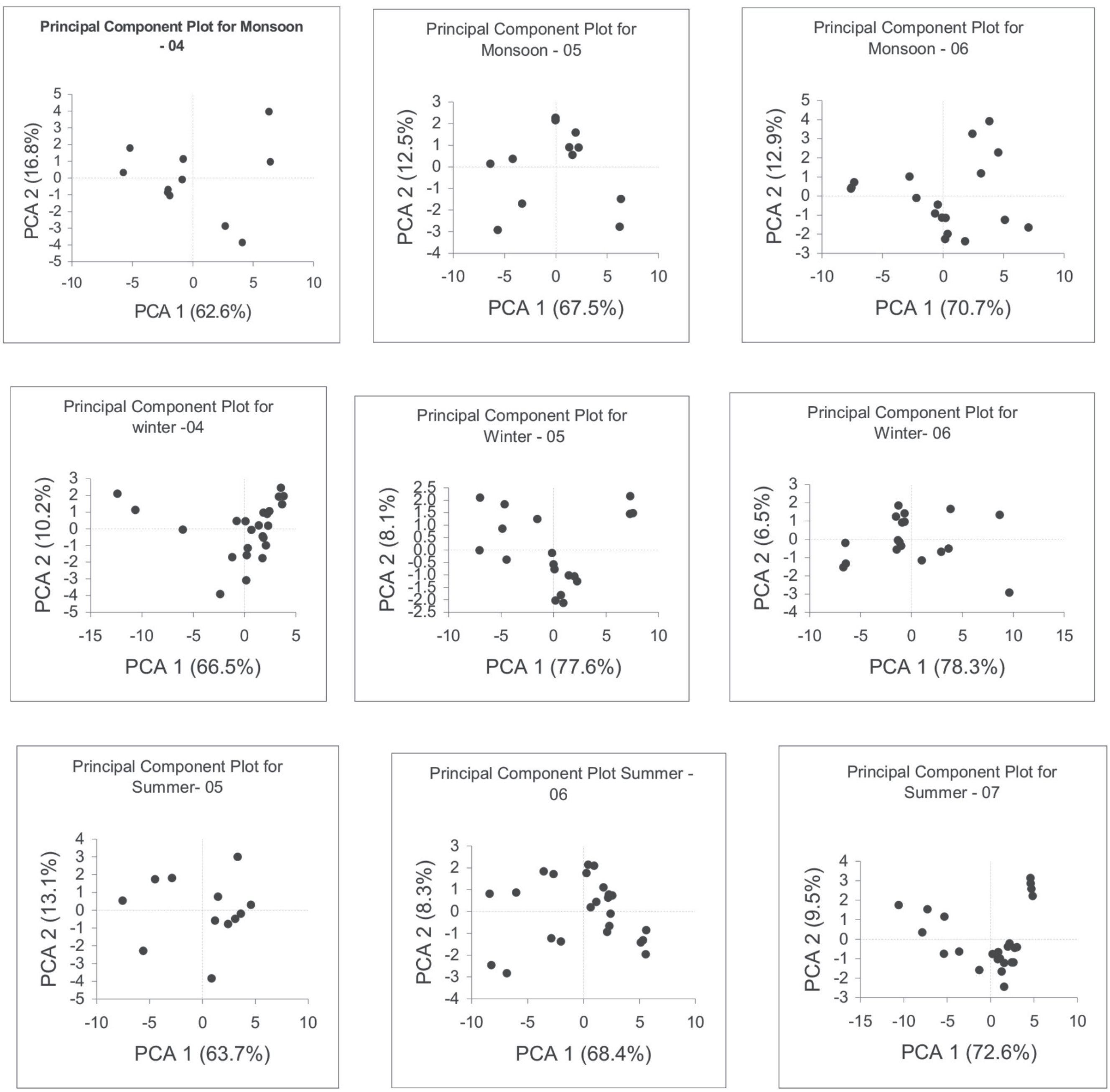

Figure 2: Component score plots of PC1 and PC2 for each season of the sampling period.

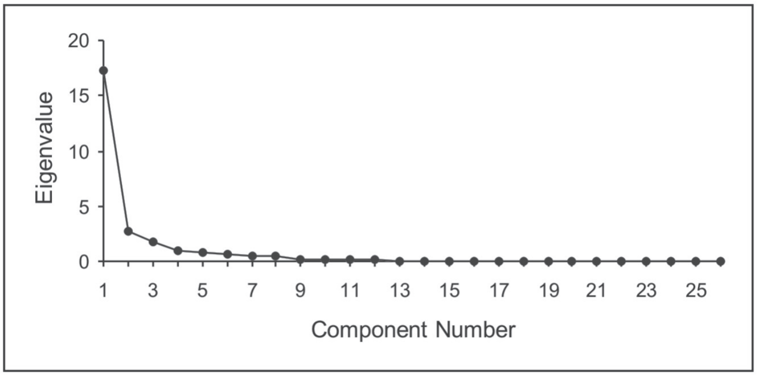

Figure 3: Scree plot of each season for the period of 2004-2007.

It implies that there was a seasonal variation in the physico-chemical character of the river water. Eigenvalues of first component for first year (Jun 2004 to May 2005) were in monsoon season (16.2), in winter season (17.2) and in summer season (16.5). For second year (Jun 2005 to May 2006) these values were in monsoon season (17.5), in winter season (20.1) and in summer season (17.7). In third year (Jun 2006 to May 2007) values were in monsoon (18.3), winter (20.3) and summer (18.8).

Data of component loading for the three years is given in Table 1. Principal components having eigenvalues greater than one were retained for this study. In the present study, it is observed that during the monsoon season of three years, the variance obtained for the retained principal components were 92.4%, 91.2% and 90.1% respectively. Most of the variables were positively loaded in PC1 for monsoon season of the year 2004 except temperature and dissolved oxygen (DO). However, during monsoon 2005, these variables were negatively loaded except temperature, pH and DO. Most of the variables again in Mon 06 were positively loaded except pH and DO.

In winter season, variances obtained was 83.7%, 90.2% and 89.7% respectively. Maximum number of variables were negatively loaded in Win-04 and Win-05 but positively loaded during Win-06 other than pH and DO. In summer season, variance obtained was 96.3%, 92.5% and 92.4% respectively. Most of the parameters were negatively loaded during the summer season of all three years. DO have positive loading in summer of each year; however pH had positive loading in Sum-06 and Sum-07, negative in Sum-05. Turbidity shows positive values of component loading in PC1 during the Sum-05 and Sum-06 but had negative in Sum-07. Phosphate had positive component loading only in Sum-05. Overall % of variance values were higher in monsoon then decreased in winter and again increased during the summer season.

Cluster Analysis

In this hierarchical cluster analysis study, squared Euclidian distance and Ward method is used to construct dendrogram. A low distance shows the two objects as similar or close together whereas a large distance indicates dissimilarity. Dendrograms of cluster analysis for different sampling stations and for the monsoon, winter and summer seasons of three years are shown in Figures 4, 5 and 6. Sampling station IV had identical cluster for all the three seasons which indicates that not appreciable variation was observed in water quality during the sampling period. Sampling stations V and VI clustered together in summer and winter seasons whereas this was not maintained in monsoon. Variation in clustering of sampling station I was observed with other locations seasonally and year-wise. Sampling location III clustered with different groups for monsoon and winter but this cluster was not retained in summer season.

Conclusion

In this study, surface water quality data for 26 physical and chemical parameters collected from six monitoring stations of Savitri river were analyzed using PCA and cluster analysis. Data shows the seasonal variation from monsoon to summer. Water Quality Index values are higher in summer season and at locations V and VI. PCA analysis demonstrated that the seasonal water quality parameter variations must be considered to evaluate the pollution load and effect of parameters on water quality because the parameter that is important in contribution of water quality for one season may not be important for other season. Cluster analysis implies that most surface water samples collected from the same location were not

Table 1: Component loading for the water quality parameters of Savitri river

Variable	*Mon 04*				*Mon 05*				*Mon 06*			*Win 04*			*Win 05*		
	PC 1	*PC 2*	*PC 3*	*PC 4*	*PC 1*	*PC 2*	*PC 3*	*PC 4*	*PC 1*	*PC 2*	*PC 3*	*PC 1*	*PC 2*	*PC 3*	*PC 1*	*PC 2*	*PC 3*
Temp	-0.381	-0.841	-0.090	-0.017	0.020	0.622	0.579	0.309	0.049	0.253	-0.440	-0.019	-0.159	0.802	-0.279	0.532	0.639
pH	0.104	0.741	0.135	0.487	0.327	0.260	0.383	-0.089	-0.774	0.512	-0.138	0.145	0.734	0.177	0.860	-0.093	0.094
DO	-0.717	0.256	-0.572	0.111	0.154	-0.855	0.418	-0.040	-0.588	0.339	0.631	0.019	0.636	0.013	0.641	0.362	0.219
Chloride	0.736	-0.397	-0.328	-0.116	-0.964	-0.009	0.017	0.186	0.936	0.201	0.058	-0.962	0.092	-0.152	-0.961	0.021	-0.060
Hardness	0.948	0.129	-0.015	-0.260	-0.951	0.075	0.078	-0.258	0.946	-0.176	-0.164	-0.967	0.062	-0.185	-0.983	-0.029	0.040
Ca	0.948	0.129	-0.015	-0.260	-0.951	0.075	0.078	-0.258	0.946	-0.176	-0.164	-0.967	0.062	-0.185	-0.983	-0.029	0.040
Mg	0.948	0.129	-0.015	-0.260	-0.951	0.075	0.078	-0.258	0.946	-0.176	-0.164	-0.967	0.062	-0.185	-0.983	-0.029	0.040
Ca-Hard	0.948	0.129	-0.015	-0.260	-0.951	0.075	0.078	-0.258	0.946	-0.176	-0.164	-0.967	0.062	-0.185	-0.983	-0.029	0.040
Mg-Hard	0.948	0.129	-0.015	-0.260	-0.951	0.075	0.078	-0.258	0.946	-0.176	-0.164	-0.967	0.062	-0.185	-0.983	-0.029	0.040
Alkalinity	0.409	0.043	0.758	0.142	-0.833	0.243	-0.408	-0.176	0.877	0.092	-0.257	-0.742	0.098	0.490	-0.934	0.067	0.059
Turbidity	0.677	-0.636	-0.151	0.045	-0.788	-0.462	-0.293	0.190	0.156	0.836	-0.448	-0.110	-0.586	-0.393	-0.895	0.259	0.149
Cond	0.965	0.001	-0.042	0.243	-0.894	-0.371	-0.026	0.080	0.898	0.382	0.191	-0.962	0.189	-0.107	-0.952	0.224	-0.056
TDS	0.965	0.001	-0.042	0.243	-0.894	-0.371	-0.026	0.080	0.898	0.382	0.191	-0.962	0.189	-0.107	-0.952	0.224	-0.056
TSS	0.965	0.001	-0.042	0.243	-0.894	-0.371	-0.026	0.080	0.898	0.382	0.191	-0.962	0.189	-0.107	-0.952	0.224	-0.056
TS	0.965	0.001	-0.042	0.243	-0.894	-0.371	-0.026	0.080	0.898	0.382	0.191	-0.962	0.189	-0.107	-0.952	0.224	-0.056
COD	0.561	-0.636	0.353	0.087	-0.676	0.653	-0.060	0.220	0.698	-0.632	0.134	-0.919	-0.207	-0.013	-0.627	-0.583	0.472
BOD	0.411	0.170	0.816	-0.107	-0.636	0.425	-0.472	-0.266	0.670	-0.650	0.107	-0.871	-0.340	0.010	-0.582	-0.682	0.376
Sulphate	0.535	-0.776	-0.037	0.289	-0.875	0.273	-0.219	0.227	0.871	0.166	-0.378	-0.753	-0.431	0.160	-0.679	-0.482	-0.412
Phosphate	0.212	-0.777	-0.006	-0.205	-0.693	0.131	0.049	0.487	0.823	0.192	0.058	-0.470	-0.142	0.461	-0.889	-0.103	-0.198
Nitrate	0.954	-0.194	-0.192	0.004	-0.897	0.317	-0.214	0.129	0.945	-0.002	-0.253	-0.957	-0.061	0.160	-0.938	-0.089	-0.117
Ammonia	0.588	0.560	-0.545	-0.018	-0.955	-0.198	0.074	0.009	0.936	0.189	0.094	-0.755	0.095	0.406	-0.959	0.053	0.110
Bromide	0.953	-0.190	-0.097	-0.015	-0.840	0.315	0.287	0.036	0.918	-0.304	-0.022	-0.892	0.264	0.167	-0.801	-0.408	0.057
Fluoride	0.967	0.149	-0.005	0.101	-0.885	0.227	0.274	0.095	0.891	-0.184	0.270	-0.939	0.118	0.158	-0.970	-0.103	0.025
MPN	0.916	0.302	-0.103	0.048	-0.707	0.116	0.595	-0.258	0.892	-0.235	0.254	-0.828	-0.371	0.186	-0.843	0.320	-0.207
Salinity	0.928	-0.023	-0.101	0.310	-0.894	-0.371	-0.026	0.080	0.898	0.382	0.191	-0.962	0.189	-0.107	-0.952	0.224	-0.056
Phenol	0.772	0.498	0.109	-0.273	-0.920	-0.265	0.234	0.091	0.833	0.428	0.315	-0.493	-0.721	0.005	-0.958	0.143	0.034
Eigenvalue	16.266	4.355	2.236	1.187	17.553	3.249	1.838	1.081	18.387	3.360	1.683	17.292	2.646	1.839	20.184	2.107	1.165
% of Var.	62.562	16.750	8.599	4.565	67.510	12.495	7.069	4.158	70.719	12.922	6.471	66.508	10.178	7.072	77.629	8.104	4.479
Cum. %	62.562	79.312	87.911	92.477	67.510	80.006	87.075	91.233	70.719	83.641	90.113	66.508	76.686	83.757	77.629	85.734	90.213

(*Contd.*)

Table 1 (*Contd.*)

Variable	*Win 06*			*Sum 05*					*Sum 06*					*Sum 07*			
	PC 1	*PC 2*	*PC 3*	*PC 1*	*PC 2*	*PC 3*	*PC 4*	*PC 5*	*PC 1*	*PC 2*	*PC 3*	*PC 4*	*PC 5*	*PC 1*	*PC 2*	*PC 3*	*PC 4*
Temp	0.147	0.777	0.520	-0.213	-0.281	-0.854	-0.335	0.145	-0.189	0.437	-0.745	0.207	0.057	-0.401	0.226	-0.690	-0.385
pH	-0.684	-0.473	0.374	-0.030	0.525	-0.535	0.051	0.631	0.699	-0.155	0.421	0.445	0.003	0.116	0.902	-0.061	-0.122
DO	-0.868	-0.070	0.135	0.312	0.627	-0.534	-0.143	-0.330	0.885	-0.264	-0.016	-0.152	0.264	0.189	0.765	0.384	0.007
Chloride	0.878	-0.227	0.329	-0.967	0.060	0.046	-0.167	-0.005	-0.783	0.226	0.058	-0.016	0.395	-0.959	0.183	0.101	-0.001
Hardness	0.959	0.090	0.140	-0.987	-0.103	0.086	-0.021	-0.035	-0.878	-0.445	-0.127	0.029	-0.102	-0.959	0.045	0.135	-0.225
Ca	0.959	0.064	0.188	-0.987	-0.103	0.086	-0.021	-0.035	-0.878	-0.445	-0.127	0.029	-0.102	-0.959	0.045	0.135	-0.225
Mg	0.959	0.064	0.188	-0.987	-0.103	0.086	-0.021	-0.035	-0.878	-0.445	-0.127	0.029	-0.102	-0.959	0.045	0.135	-0.225
Ca-Hard	0.959	0.064	0.188	-0.987	-0.103	0.086	-0.021	-0.035	-0.878	-0.445	-0.127	0.029	-0.102	-0.959	0.045	0.135	-0.225
Mg-Hard	0.959	0.064	0.188	-0.987	-0.103	0.086	-0.021	-0.035	-0.878	-0.445	-0.127	0.029	-0.102	-0.959	0.045	0.135	-0.225
Alkalinity	0.900	-0.117	-0.207	-0.369	0.634	0.409	0.431	-0.150	-0.841	0.307	0.328	0.066	0.109	-0.683	-0.550	0.022	0.036
Turbidity	0.778	-0.027	-0.087	0.075	-0.632	-0.296	0.663	0.077	0.117	0.109	0.127	0.880	-0.140	-0.731	0.239	-0.179	0.546
Cond	0.942	-0.277	0.059	-0.985	0.037	0.087	-0.109	0.054	-0.950	-0.098	0.075	-0.001	0.271	-0.968	0.216	-0.037	0.053
TDS	0.942	-0.277	0.059	-0.985	0.037	0.087	-0.109	0.054	-0.950	-0.098	0.075	-0.001	0.271	-0.969	0.215	-0.037	0.053
TSS	0.942	-0.277	0.059	-0.985	0.037	0.087	-0.109	0.054	-0.950	-0.098	0.075	-0.001	0.271	-0.969	0.215	-0.037	0.053
TS	0.942	-0.277	0.059	-0.985	0.037	0.087	-0.109	0.054	-0.950	-0.098	0.075	-0.001	0.271	-0.969	0.215	-0.037	0.053
COD	0.979	-0.061	-0.087	-0.870	-0.302	-0.087	0.190	-0.153	-0.853	0.228	-0.315	-0.086	-0.264	-0.950	-0.121	0.060	-0.030
BOD	0.918	-0.235	-0.212	-0.891	-0.242	-0.067	0.179	-0.134	-0.797	-0.227	-0.052	0.211	-0.300	-0.956	-0.041	0.061	0.009
Sulphate	0.786	0.166	-0.468	-0.896	-0.369	-0.157	-0.069	0.140	-0.855	0.381	0.224	-0.005	0.012	-0.875	-0.217	-0.283	-0.142
Phosphate	0.810	0.317	0.105	0.093	-0.756	-0.278	0.550	-0.064	-0.847	0.195	0.361	-0.060	-0.061	-0.869	-0.067	-0.040	0.202
Nitrate	0.948	0.161	-0.062	-0.684	0.491	-0.386	0.329	-0.072	-0.955	0.095	0.154	0.069	0.008	-0.923	-0.239	-0.190	0.010
Ammonia	0.837	0.202	-0.283	-0.687	0.360	-0.375	0.279	-0.306	-0.713	0.477	-0.136	-0.178	-0.194	-0.820	-0.256	-0.437	-0.013
Bromide	0.908	0.197	0.054	-0.581	0.321	0.331	0.455	0.448	-0.905	0.266	-0.141	-0.022	-0.170	-0.520	-0.322	0.660	-0.140
Fluoride	0.925	0.074	-0.177	-0.593	0.646	-0.243	0.274	-0.002	-0.925	0.239	0.128	0.054	-0.189	-0.964	0.017	0.111	-0.061
MPN	0.917	-0.103	0.310	-0.899	0.000	-0.264	-0.187	-0.261	-0.915	0.196	-0.033	0.155	0.045	-0.806	0.150	0.008	0.511
Salinity	0.942	-0.277	0.059	-0.985	0.037	0.087	-0.109	0.054	-0.950	-0.098	0.075	-0.001	0.271	-0.968	0.217	-0.036	0.052
Phenol	0.828	0.258	-0.224	-0.902	-0.206	-0.089	-0.192	0.193	-0.219	-0.035	0.541	-0.337	-0.494	-0.856	-0.250	0.160	0.268
Eigenvalue	20.347	1.680	1.314	16.555	3.405	2.283	1.765	1.047	17.796	2.169	1.623	1.280	1.191	18.868	2.464	1.557	1.146
% of Var.	78.258	6.460	5.052	63.675	13.094	8.779	6.787	4.026	68.447	8.343	6.242	4.922	4.580	72.568	9.476	5.988	4.410
Cum. %	78.258	84.718	89.770	63.675	76.769	85.548	92.335	96.362	68.447	76.790	83.031	87.954	92.534	72.568	82.045	88.032	92.442

(Temp - Temperature, DO - Dissolved Oxygen, TDS - Total Dissolved Solid, Cond - Conductance, TSS - Total Suspended Solids, TS - Total Solids, COD - Chemical Oxygen Demand, BOD - Biochemical Oxygen Demand, MPN - Most Probable Number, Mon - Monsoon, Win - Winter, Sum - Summer, 04, 05, 06, 07-Year 2004, 2005, 2006, 2007)

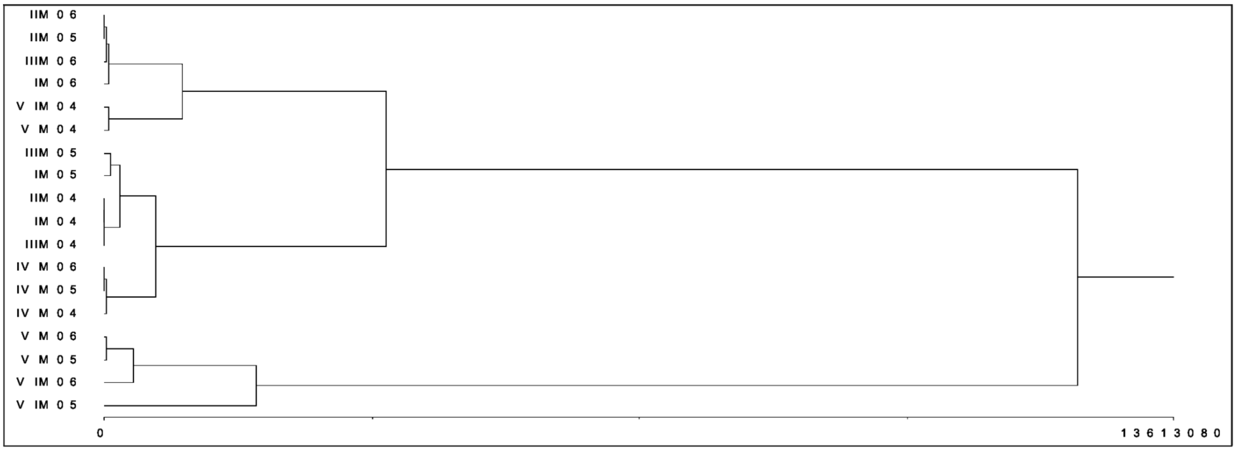

Figure 4: Dendrogram of hierarchical cluster analysis for monsoon season of three years. (I, II, . . . Sampling Stations, M - Monsoon, W - winter, S - Summer and 04, 05, 06 - year 2004, 2005, 2006)

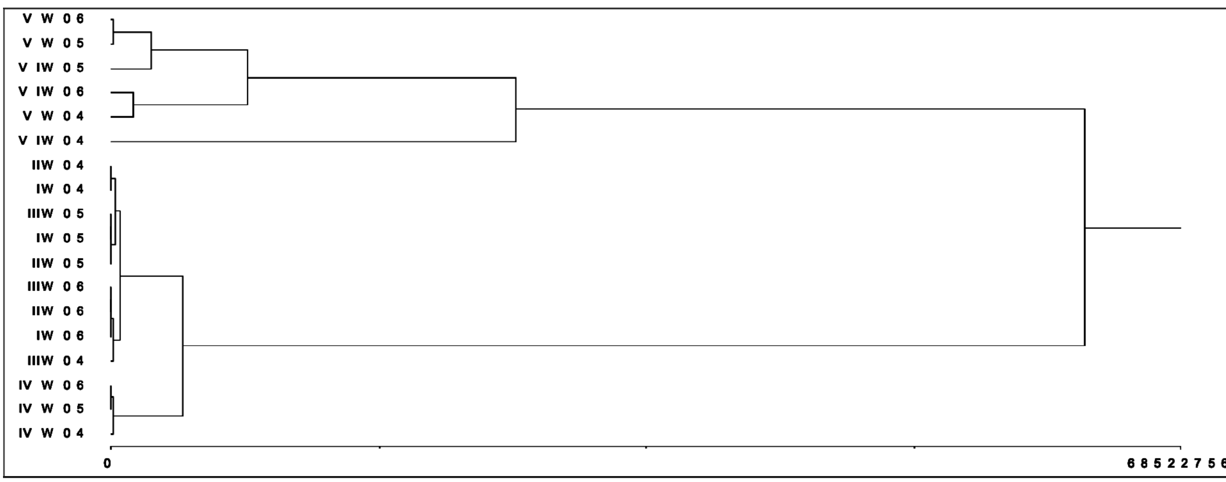

Figure 5: Dendrogram of hierarchical cluster analysis for winter season of three years.

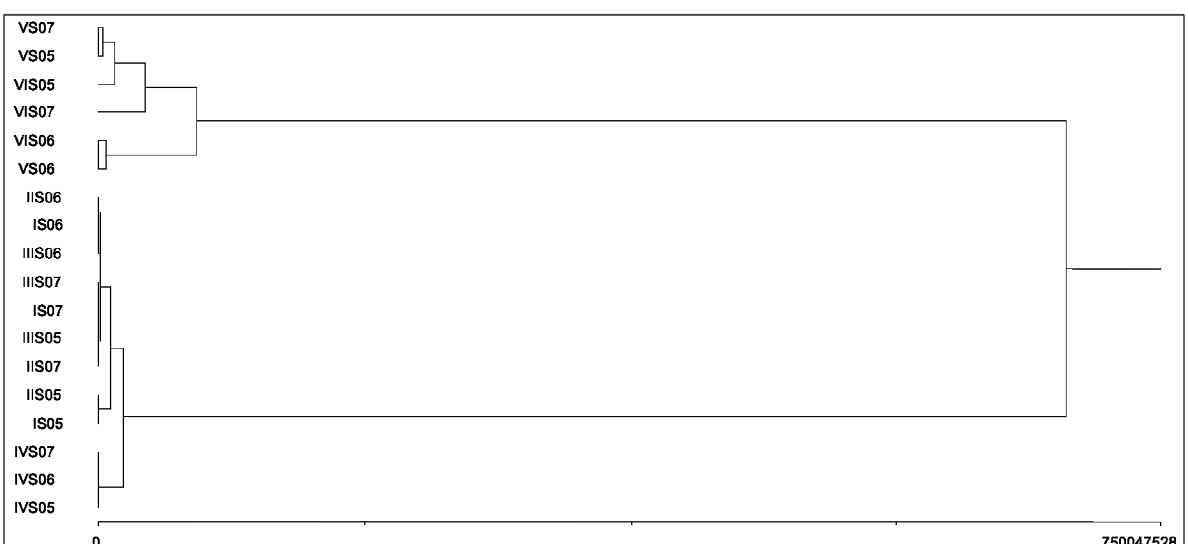

Figure 6: Dendrogram of hierarchical cluster analysis for summer season of three years.

clustered together especially for summer season and this demonstrates that Savitri river water characters change significantly with seasons.

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