Surface Water Quality Assessment of River in South India Using Multivariate Statistical Methods

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Abstract:

The objective of present study is to identify Physico-chemical parameters that are more important in assessing annual variations of river water quality. Eight Physico-chemical parameters (Atmospheric Temperature, Water Temperature, pH, Dissolved oxygen, Total Alkalinity, Chloride, Total phosphorus and Ammonia–nitrogen) were used for monitoring water quality of River in South India (Karnataka state) in the period of June (2005) to May (2006). The dataset was treated using correlation matrix and principle component analysis. Correlation matrix revealed that a high positive correlation (0.780) exist between Atmospheric Temp and Water Temp; DO and Cl_2 are negatively correlated (-0.664), and there is hardly any correlation between PO_4-P and NH_4-N; Cl_2 and TA respectively. PCA results show that 4 Physico-chemical parameters (Atmospheric Temperature, Water Temperature Dissolved oxygen and Chloride) identified as more important in explaining the annual variance of data set. The first component called the natural factor explained 44.179% of the total variance. The second factor named the anthropogenic factor explained 42.556%. Regression analysis also proved that the 4 Physico-chemical parameters Atmospheric Temp and Water Temp; DO and Cl_2 are principal parameters which are mainly responsible for quality of river water. Since the addition of data of remaining 4 Physico-chemical parameters did not improve the curve-fitting.

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1. Introduction:

Lakes and rivers have important multi-usage components, such as sources of drinking water, irrigation, fishery and energy production. These considerably depend on water quality and thus water quality should be kept at a certain level. Surface water quality is controlled by complex anthropogenic activities and natural factors (Jian Zhao et al. 2011; Jarvie et al. 1998; Ravichandran, 2003). As a responsible citizen and scientist of India we must make sure that our water resources remain minimum polluted. So there is a need to develop a systematic program to clean the above set pollution present almost in every river water. It is imperative to prevent and control the rivers pollution and to have reliable information on the quality of water for effective management. In view of the variations in the hydrochemistry of rivers, regular monitoring programs are required for reliable estimates of the water quality. The first step is to collect the data base of polluted water in terms of Physico- chemical parameters and then analyze the data so that with minimum money we could clean the polluted river water.

Accurate assessment of the type and extension of water pollution is a difficult task (Huang et al., 2010). A stricter standard for drinking water quality made by the National Standardization Committee and Ministry of Public Health was effective in 2007 (Zhi-wei ZHAO and Fu-yi CUI 2009; Zhang et al.2007). Therefore, the reconstruction of these water treatment plants must be considered. A particular problem in the case of water quality monitoring is the complexity associated with analyzing the number of measured variables. The data set contain rich information about the behavior of the water resources. Classification, modeling and interpretation of monitored data are the most important steps in the assessment of water quality (Cansu Filik Iscen et al.2008) Boyacioglu 2006).

Multivariate statistical methods have been widely applied to investigate environmental phenomena in recent years (Laaksoharju et al., (1999); Anazawa et al., (2003); Gűler and Thyne, (2004); Anazawa and Ohmori, (2005)). They include cluster analysis, principle component analysis/factor analysis, time series analysis, self-organizing maps and classification and regression trees (CART) strategy, etc., and are a powerful tool for deriving useful information from complicated data about water quality studies (Vega et al., 1998; Helena et al., 2000; Bengraine and Marhaba, 2003; Liu et al., 2003; Simeonov et al., 2003; Simeonova et al., 2003; Simeonova and Simeonov, 2006; Astel et al., 2007; 2008). The multivariate statistical methods have an extensive application in characterization and evaluation of surface water quality and are useful for evaluation of temporal and spatial variations caused by natural and anthropogenic factors (Vega et al.1998; Reisenhofer, et al.1998; Singh et al.2004; 2005).We are presenting a case study of River[27] near Gulbarga city of Karnataka state, in India in which the Physico-chemical parameters like: Atmospheric temperature, water temperature, pH, DO (dissolved oxygen), TA (total alkalinity), Cl_2, PO_4-P, NH_4-N were analyzed by multivariate statistical methods.

2. Materials and Method:

In this study, eight 8 Physico-chemical parameters obtained from River at Karnataka. The investigations of Physico-chemical parameters were carried out during June 2005 to May 2006. The water samples were collected on monthly basis during 9 AM to 11 AM and brought to laboratory for the further analysis and analyzed for Physico-chemical parameters, following the standard method (APHA, 1985). All the samples were analyzed for Atmospheric Temperature (Atm. Temp) (^{0}C) Water Temperature (Water Temp), pH, DO (mg/l) (dissolved oxygen), total alkalinity (TA) (mg/l), Cl_2 (mg/l) PO_4-P (mg/l) NH_4-N (mg/l) were enumerated using the most probable number technique (MPN) (APHA 1992). River water quality data set were subjected to three multivariate techniques: Correlation matrix (CM), Principal Component Analysis (PCA) and Regression analysis (RA). All mathematical and statistical computations were made using SPSS 18.0, Origin 6.1and Microsoft Office Excel 2007.

PCA was performed in this study to identify the potential for reducing the number of Physico chemical parameters of river water and also for providing information regarding the most meaningful parameters, which describe whole data set, rendering for data reduction with minimum loss of original information (Vega et al. 1998; Wunderlin et al.2001). It is a powerful technique for pattern recognition and attempts to explain the variance of a large set of inter-correlated variables and transform it into a smaller set of independent variables (Shrestha and Kazama, 2007). Eight water quality parameters from 12 months were examined in this study. The procedures used for PCA is described below. The aim of this study is to apply the PCA technique in the evaluation of correlations of water quality parameters, and to extract those parameters most relevant to assessing variations in river water quality.

Table 1: The water quality parameters associated with their abbreviations and units used in this study and univariate statistics corresponding to the total samples analyzed

Parameters	Abbreviation	Unit	Range	Mean	Std. Deviation
Atmospheric Temperature	At Temp	^{O}C	9.20	28.9250	2.80037
Water Temperature	Wt Temp	^{O}C	8.20	23.5167	2.27070
pH	pH	pH units	1.00	8.2917	.30883
Dissolved oxygen	DO	mg/l	5.40	3.8000	1.48017
Total Alkalinity	TA	mg/l	68.00	146.8333	22.85063
Chloride	Cl_2	mg/l	29.30	48.8917	11.63850
Total phosphorus	PO_4P	mg/l	0.06	0.1342	0.01929
Ammonia–nitrogen	NH_4N	mg/l	0.40	0.5192	0.16362

3. Results and discussion:

3.1 Correlation of water quality parameters

Data in Table 2 provide the different paired samples Correlations of river water quality parameters obtained from the PCA. Few pairs exhibiting significant correlation relationships are highlighted.

The correlation coefficients between Atm. Temp and other parameters were less than or equal to 0.55 except with Water Temp (0.780). There is a negative correlation between Atm. Temp with pH, Cl_2, PO_4 - P ; Water Temp with pH, TA, Cl_2, PO_4 -P and pH with DO respectively. A negative correlation is also shown by DO with Cl_2 (-0.664), PO_4 -P There is hardly any correlation exists between Cl_2 and TA; NH_4-N and PO_4 -P.

It is interesting to observe that a high positive correlation (0.780) exist between Atm. Temp and Water Temp. Dissolved Oxygen and chloride shows negative correlation (-0.664). (Karunakaran et al. 2009; Patil and Patil 2010) Different types of correlations are shown in Fig. 1, 2, .3 and 4 respectively.

Table 2 Different Paired Samples Correlations of River, Karnataka 2005

		r	t	Sig.
Pair 1	**At Temp & Wt Temp**	**0.780**	**10.671**	**0.003**
Pair 2	**At Temp & pH**	-.333	24.497	.290
Pair 3	**At Temp & DO**	.351	32.609	.263
Pair 4	**At Temp & TA**	.012	-17.769	.969
Pair 5	**At Temp & Cl_2**	-.442	-5.272	.150
Pair 6	**At Temp & PO_4P**	-.376	35.522	.229
Pair 7	**At Temp & NH_4N**	-.058	34.960	.857
Pair 8	**Wt Temp & pH**	-.354	21.999	.259
Pair 9	**Wt Temp & DO**	.229	28.334	.475
Pair 10	**Wt Temp & TA**	-.197	-18.252	.539
Pair 11	**Wt Temp & Cl_2**	-.220	-7.124	.491
Pair 12	**Wt Temp & PO_4P**	-.454	35.533	.138
Pair 13	**Wt Temp & NH_4N**	.137	35.343	.671
Pair 14	**pH & DO**	-.416	9.529	.179
Pair 15	**pH & TA**	.022	-21.007	.947
Pair 16	**pH & Cl_2**	.312	-12.181	.324
Pair 17	**pH & PO_4P**	.479	94.174	.115
Pair 18	**DO & TA**	.228	-21.963	.477
Pair 19	**DO & Cl_2**	**-0.664**	**-12.328**	**0.018**
Pair 20	**DO & PO_4P**	-.252	8.551	.430
Pair 21	**DO & NH_4N**	.122	7.735	.707
Pair 22	**TA & Cl_2**	.099	13.795	.759
Pair 23	**TA & PO_4P**	.573	22.250	.051
Pair 24	**TA & NH_4N**	.445	22.251	.147
Pair 25	**Cl_2 & PO_4P**	.300	14.519	.343
Pair 26	**Cl_2 & NH_4N**	.278	14.453	.381
Pair 27	**PO_4P & NH_4N**	.085	-8.176	.793

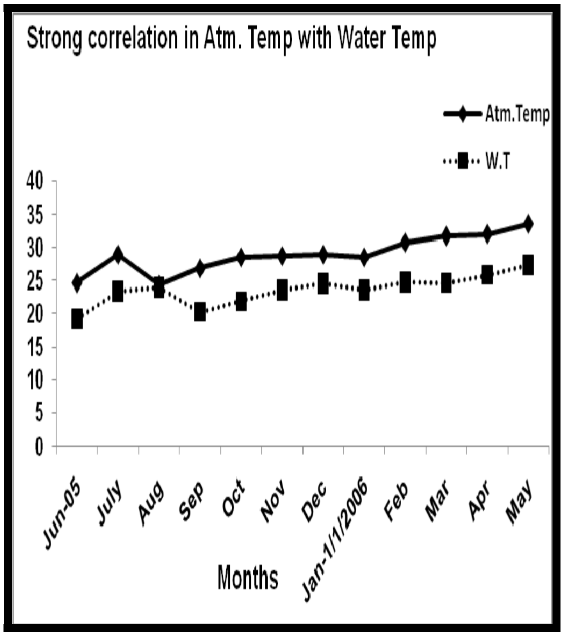


Fig 1- Showing Strong correlation in Atm. Temp with Water Temp

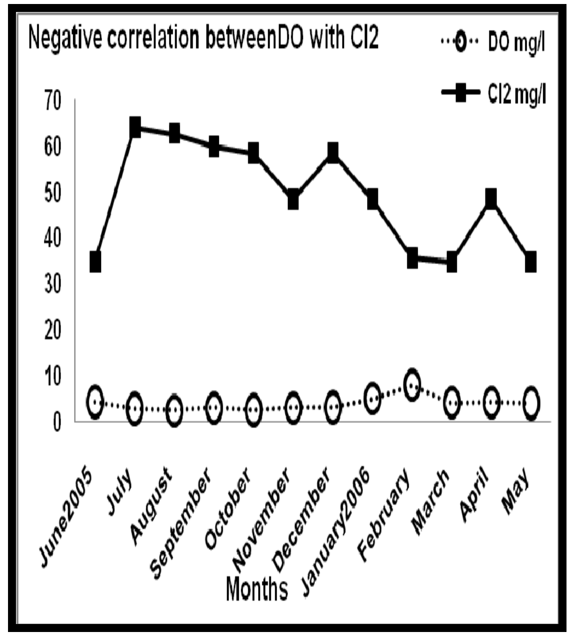


Fig 2- Showing negative correlation in DO with Cl_2

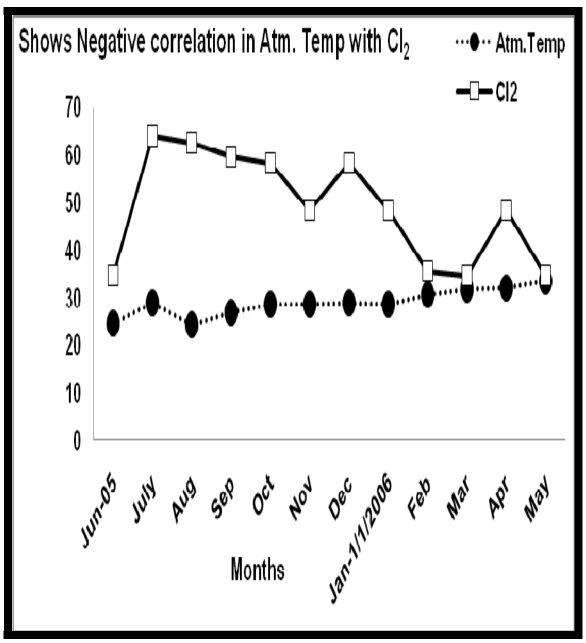


Fig 3- Showing negative correlation in Atm. Temp with Cl_2

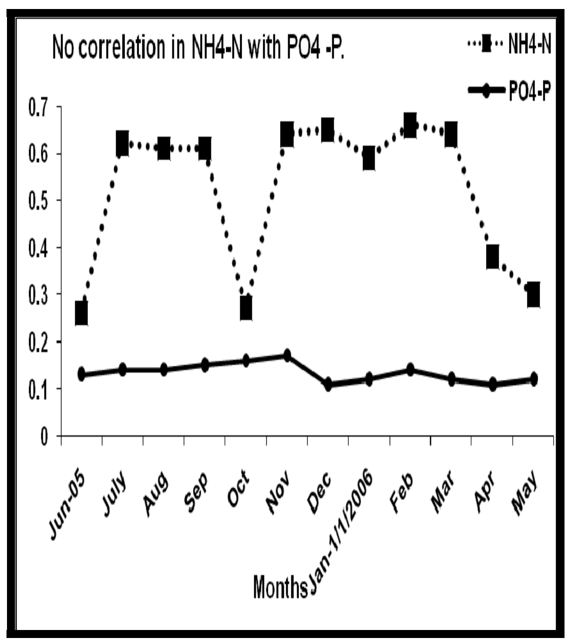


Fig 4 - Showing no correlation in NH_4-N with PO_4 -P

3.2 PCA of water quality parameters

Table 1 shows some of the statistics derived from the univariate analysis. PCA was actually performed on the correlation matrix between the different parameters followed by Varimax rotation, with the same being used to examine the association between them (Kuppusamy and Giridhar 2006). Eigenvalues greater than 1 were taken as criterion for extraction of the principal components required to explain the sources of variances in the data. The scree plot is shown in Fig. 5.

Fig. 5 Scree plot

Scree plot shows eigen value for each component. Plot shows that first three eigen values are significant. Thus first three PCs are the most significant components. Which represent more than 74.689% of the variance in water quality of River is shown in Table 3.1

The objective of this analysis was primarily to create an entirely new set of variates or factors much smaller in number when compared to the original data set of variables for inclusion in subsequent analysis. The eigenvalues for different factors, percentage variance counted, cumulative percentage variance and component loadings (unrotated and Varimax rotated) are given in Table 3.1. The principal components, PC-1, PC-2 and PC-3 contribute about 74.689% of the total variance in the data. 28.361% by PC1, 24.824% by PC2 and 21.504% by PC-3;

Table 3.1 Results of Principal component Analysis

Component	Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Eigen value	% of Variance	Cumulative % variance	Eigen value	% of Variance	Cumulative % variance
1	3.046	38.078	38.078	2.269	28.361	28.361
2	1.692	21.147	59.225	1.986	24.824	53.185
3	1.237	15.464	74.689	1.720	21.504	74.689

Extraction Method: Principal Component Analysis.

Table 3.2 Varimax Rotated Component Matrixes

Parameters	Components		
	1	2	3
Wt Temp	**.924**	-.074	.061
At Temp	**.753**	-.361	.068
PO_4-P	-.683	.159	.469
Cl_2	-.139	**.863**	.230
DO	.186	**-.861**	.220
pH	-.447	.491	.101
TA	-.283	-.220	**.860**
NH_4-N	.219	.223	**.800**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization. Values above 0.7 have been considered.

Table 4.1 Results of Principal Component Analysis

Components		Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
		Eigen value	% of Variance	Cumulative % variance	Eigen value	% of Variance	Cumulative % variance
	1	2.353	58.817	58.817	1.767	44.179	44.179
	2	1.117	27.918	86.734	1.702	42.556	86.734

Confirming the results of the PCA(Garcia-Montelongo F. et al. 1994; RSS SPSS Short Course Module 9, 2012), the Varimax rotated matrix in table 3.2 show that variable (Atmospheric Temperature, Water Temperature Dissolved oxygen and Chloride) mainly have strong loadings on component 1 and component 2 respectively and in PC-3 variable TA and NH_4-N are highly loaded but after calculating the different Paired Samples correlations given in table-2 we found there is hardly any correlation exists between TA and NH_4-N ($r=0.445$, $p=0.147$). Thus for the second trial of PCA we consider only the 4 variables which are showing (At Temp & Wt Temp r= 0.780) (DO & Cl_2 r=-0.664) higher level of significance. Table 4.1 shows that new PCA indicates that two principal components which we got explain the 86.734% of the total variance Principal Component 1 accounting for 44.179% of the total variance Principal Component 2 , accounts for 42.556% of total variance Table 4.2 shows that PC1constitutes Wt Temp and At Temp while PC2 constitutes DO and Cl_2 .

Table 4.2 Varimax Rotated Component Matrix

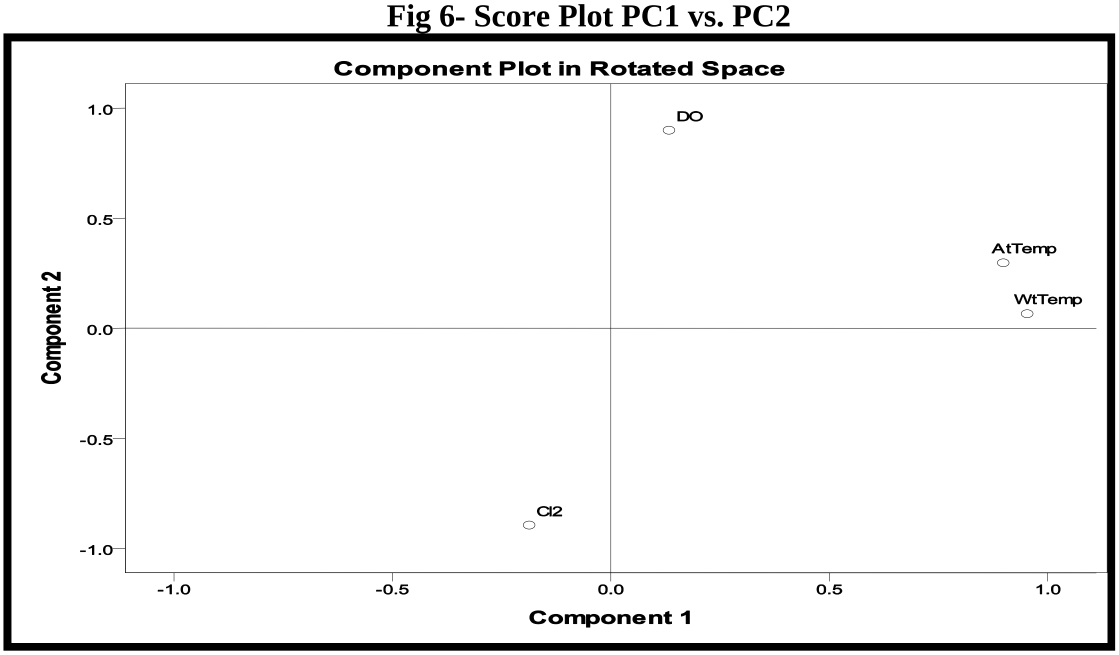
	Component	
	1	**2**
Wt Temp	.953	
At Temp	.898	
DO		.900
Cl2		-.895

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

PC1 named natural factor, is impacted by seasonal changes (Singh et al. 2005). The highest burden in this component was revealed by Water Temperature and Atmospheric Temperature. It revealed that intensive pollution had occurred into the river due to the various climate conditions or variation in weather. (Main reason also for these global warming, air pollution and anthropogenic sources)

Principal Component 2 namely anthropogenic factor, accounting for 42.556% of total variance and had strong positive loading on Dissolved Oxygen and strong negative loading on Cl_2. Man-made pollution was demonstrated to originate from municipal wastewater discharged into the river. Table.4.2 shows there exist negative correlation between DO and Cl_2. When there are high concentrations of Dissolved oxygen in the water, there is lower concentration of Cl_2 in the water. This is because the quantity of dissolved oxygen in water is directly or indirectly dependent on water temperature, partial pressure of oxygen in the air and the amount of salinity (sodium chloride, magnesium, or calcium sulfates.) (Welch, 1952) and (Wetzel, 1975). i.e. the amount of salts dissolved in a body of water. The chloride concentration serves as an indicator of pollution by sewage. People accustomed to higher chloride in water are subjected to laxative effects studied by (Dahiya and Kaur 1999), large content of chlorides in freshwater are an indication of organic pollution, harms metallic pipes in water bodies and also harmful for agriculture crops (Suresh et al., 1992; Tharsh et al.1994). Though chloride levels as high as 250 mg/l is safe human consumption, a level above this imparts salty taste to potable water. Low values may be affecting the fish life in aquatic system (Siddiqui 2002).

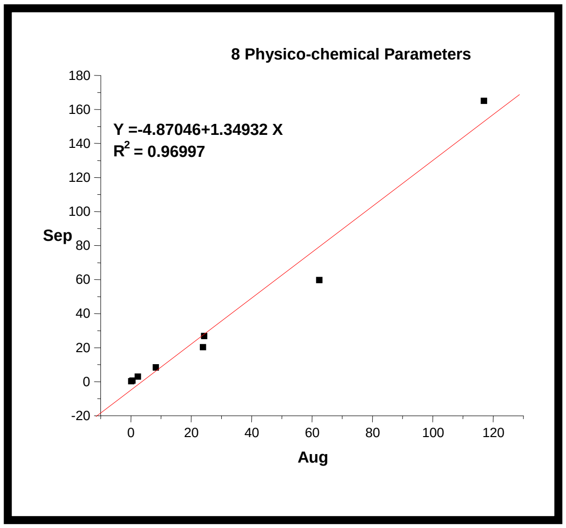
Fig 6- Score Plot PC1 vs. PC2

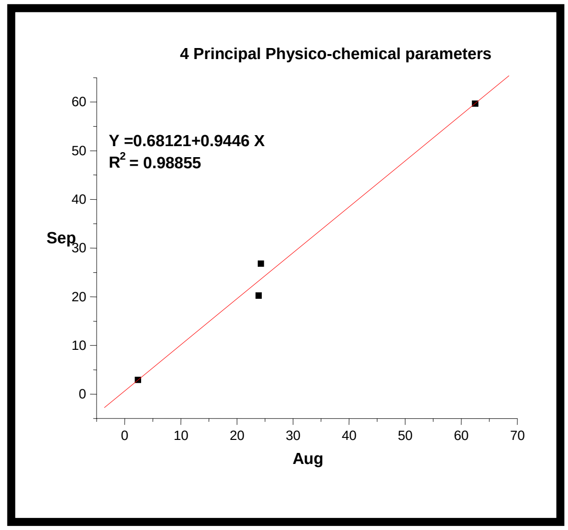


Score plot shown in fig 6. also shows that PC1 is constituted by(Atmospheric Temperature, Water Temperature) while PC2 is constituted by Dissolved oxygen and Chloride.

Validation of PCA Results

The following relationship formulate by regression analysis: August versus September. In this data with all of the Physico-chemical parameters (i.e., highly loaded and less loaded parameters) were used to formulate the relationship by regression analysis. This case was then compared to determine if the of data from the 4 highly loaded parameters improved the regression relationships. Comparison of the relationship between August and September obtained using data of all the 8 physicochemical parameters (Fig 7a) with that obtained using data of rest of four highly loaded physicochemical parameters of (Fig.7b) showed that the addition of the four less loaded parameters did not improve the curve fitting between September (Y) and August (X), as indicated by correlation coefficients (i.e., R^2 values).The R^2 value for the regression equation (Y = 4.87046+1.34932 X) data of all the 8 physicochemical parameters was 0.96997, whereas the R^2 value for the regression equation (Y = 0.68121+0.9446 X)for data of the 4 principal parameters was 0.98855. The latter is slightly better than the former. Therefore, the 4 Physico-chemical parameters (WT, AT, DO and Cl_2) are considered to be principal parameters since the addition of non principal Physico chemical parameters data (PO_4-P, pH, NH_4-N, TA) did not improve the curve-fitting.





(A) **(B)**

Fig. 7.Relationship between August and September for data of all the parameters (A), Relationship between June 2005 and July for data of 4 principal parameters (B).

Summary and Conclusions:

This study concludes the usefulness of multivariate statistical assessment of dataset in order to obtain better information concerning the quality of surface water. In this case study, different multivariate statistical techniques were used to evaluate variations in the surface water quality of the River. Analysis of our results revealed that the River carried high loads of Atmospheric Temperature, Water Temperature, DO and Cl_2.

1) The outcome showed that there was a potential for improving the efficiency and economy of the monitoring network in the River in Karnataka by reducing the number of monitoring parameters from 8 to 4. This reduction may result in significant cost savings without sacrificing important river water quality data.

2) In this study, water quality data for 8 physical and chemical parameters were collected on monthly basis along the River at Karnataka in India from months June (2005) to May (2006) were analyzed, using the PCA and Regression analysis technique.

3) The correlation coefficients between Atm. Temp and other parameters were less than or equal to 0.55 except for Water Temp (0.780). There is a negative correlation between At. Temp and pH, Cl_2, PO_4 – P; Wt Temp and pH, TA, Cl_2, PO_4 – P; pH and DO respectively. A negative correlation is also shown by DO with Cl_2, PO_4-P.

4) It is interesting to observe that a high positive correlation (0.780) exist between At. Temp and Wt Temp while DO and Cl_2 are negatively correlated, and there is hardly any correlation between PO_4-P and NH_4-N; Cl_2 and TA respectively.

5) PCA results show that 4 Physico-chemical parameters (Atmospheric Temperature, Water Temperature Dissolved oxygen and Chloride) identified as more important in explaining the annual variance of data set, and therefore could be principal parameters. While remaining four parameters (PO_4-P, pH, NH_4-N, TA) are the non principal parameters. The first component named as the natural factor explained 44.179% of the total variance. The second factor named the anthropogenic factor explained 42.556% respectively. Regression analysis also proved that the 4 Physico-chemical parameters Atmospheric Temperature, Water Temperature Dissolved oxygen and Chloride are considered to be principal parameters. Since the addition of data of non principal 4 Physico-chemical parameters did not improve the curve-fitting.

6) The outcome shows there is a potential for improving the efficiency and economy of the monitoring network in river at Karnataka by reducing the number of Physico- chemical monitoring parameters of water quality from 8 to 4. This reduction may result in significant cost saving in monitoring program without sacrificing important river water quality

7) However it should be noted that only one year annual mean values of water quality parameters were used in this study. Prior to making any critical decision in eliminating water quality Physico-chemical parameters of river in south , the PCA with longer time scale(ie more than 3 years) should be performed.

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