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## RESEARCH ARTICLE

### CHEMOMETRIC ASSESSMENT OF SURFACE WATER QUALITY IN VAIGAI RIVER, SOUTH INDIA

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#### ABSTRACT

Chemometric statistical techniques were applied for the evaluation and interpretation of a large complex water quality data set of Vaigai river in South India, monitoring 20 parameters at four different sites in quarterly basis. Principal component analysis resulted in three principal components (PC) explaining 99.9% of the total variance in water quality. The factors indicate that the possible variances in water quality may be due to either sources of anthropogenic origin or due to different biochemical processes that are taking place in system. All datasets were subjected to compute correlation and water quality index (WQI). WQI exceeded WHO permissible limit of 100, indicating that the water samples were unfit for human consumption, rearing of wild life and can be used for irrigation. Regression analysis revealed greater influence of alkalinity and BOD in determination of WQI. This study illustrates the benefits of Chemometric statistical techniques for determination of water quality.

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## INTRODUCTION

Rivers are among the most vulnerable water bodies to pollution because of their role in carrying municipal and industrial wastes and run-offs from agricultural lands in their vast drainage basins. They constitute the main inland water resources for domestic, industrial and irrigation purposes; it is inevitable to prevent and control the river pollution and to have reliable information on quality of water for effective management. The rapid urbanization coupled with increasing discharge from industrial, domestic and agricultural actions into the surface water regime, is a serious cause of concern. Other possible variances in water quality may be due to anthropogenic activities, natural variances during months (season) due to various biochemical or chemical processes (Liu *et al.*, 2011). The quality of water may be described according to their physico-chemical and micro-biological characteristics. Monitoring programs result in a huge and complex data matrix consist of a large number of physico-chemical parameters (Chapman, 1992). The application of multivariate methods such as Cluster analysis (CA), principal component analysis (PCA), has increased tremendously in recent years for analyzing environmental data and drawing meaningful information (Boyacioglu and Boyacioglu, 2010; Bulut *et al.*, 2010; Chatterjee *et al.*, 2010; Odjadjare and Okoh, 2010; Palma *et al.*, 2010; Schaefer and Einex, 2010; Solanki *et al.*, 2010; Ghuman, 2011; Juahir *et al.*, 2011; Kannel *et al.*, 2011; Lopez-Lopez *et al.*, 2011; Prikler *et al.*, 2011; Sarukkalige, 2011; Song *et al.*, 2011; Wang *et al.*, 2011). These techniques permit identification of the possible factors/sources that influence the water systems and are responsible for the variations in water quality, which thus

offers valuable tool for developing appropriate strategies for effective management of the water resources (WHO, 1984). With the increase in water quality degradation and lack of regular monitoring program, the Vaigai River in Madurai city is heading towards disaster. In view of the present situation and evaluation of a comprehensive monitoring plan, the present study was taken up. The overall aim of the investigation was to analyze the water quality data of Vaigai River in the sampling stations using statistical tools like Correlation, Water Quality Index, Regression, Principal Component Analysis and Cluster Analysis, and hence reduce the number of data and similar groups/clusters creating, that may help efficient monitoring and identifying the pollution sources.

## MATERIALS AND METHODS

### Study area and sampling sites

Vaigai River (9<sup>o</sup>20'60N, 79<sup>o</sup>0'0E) selected for this study flows in the southern part of India, in the state of Tamil Nadu. All major water supply schemes have been formulated with Vaigai River as the source of municipal water supply to Madurai city. Selection of sampling stations along its stretch was based on degree of exposure to human impact and its connectivity to Madurai city.

### Analytical methods

Surface waters were collected from the selected sampling stations on quarterly basis from May 2009 to April 2010. Water analysis including the sample collection, was carried out according to the standard methods (APHA, 2005).

Physical parameters like pH and temperature were carried out at the field sites itself. Analytical grade chemicals and double distilled water were used for preparing solutions for analysis. The parameters included pH, temperature(T), Alkalinity (Alk), Total solids(TS), Total dissolved solids(TDS), Total suspended solids(TSS), Chloride(Cl<sub>2</sub>), Dissolved oxygen (DO), Chemical oxygen demand (COD), Biological Oxygen demand (BOD), Inorganic phosphorous (PO<sub>4</sub>), Nitrate (NO<sub>3</sub>), Calcium (Ca), Sodium (Na), Potassium(K), Chlorophyll a (Chl) and Phycobilins (Phy). Cyanobacterial cell density, fecal coliforms and fecal streptococci count were also determined by using hemocytometry, membrane filter technique and MPN index respectively. Microcystin concentration in the water sample was determined by using ELISA quantiplate kit for microcystin (Envirologix, USA).

### Data Computation

Karl-Pearson correlation coefficient ( $r$ ) between physico-chemical variables was calculated and correlation for significance was tested by applying  $t$ -test. Principal component analysis (PCA) was used for orthogonal linear transformations of the experimental data to new Coordinate system such that the greatest variance by any projection of the data comes to lie on the first coordinate (called the first principal component), the second greatest variance on the second coordinate, and so on. It was also used for dimensionality reduction in a data set by retaining those characteristics of the data set that contribute most to its variance, by keeping higher-order principal components and ignoring lower-order ones. Bray-Curtis cluster analysis was done to find the similarity in physico-chemical profile among the sampling stations. Out of thirteen parameters studied nine were taken for calculating the water quality index (Harkins, 1974; Naik and Purohit, 1996; Tiwari and Manorama, 1985; Ramakrishnaiah *et al.*, 2009). Regression analysis was done to confirm the effect of individual physico-chemical parameter on determination of water quality index.

## RESULTS AND DISCUSSION

The computed data were subjected to descriptive statistical analysis and subsequent correlation analysis; followed by chemometric techniques and water quality index. The correlation matrix of the Vaigai river samples (Table 1) exhibited excellent positive correlation values between TDS and chloride, calcium, nitrate. This is due to the fact that the main constituents of TDS in water are nitrate, calcium and chloride. A complete positive correlation was observed between inorganic phosphorous and nitrate with alkalinity, BOD and phycobilin. This is supported by the fact that an increase in the nitrate and inorganic phosphorous content of water positively favors the growth of cyanobacteria which is ultimately reflected in an increase in alkalinity, BOD and phycobilin content of water samples. A significant negative correlation was noticed among chlorophyll a content with dissolved oxygen and inorganic phosphorous content in water sample, which is possibly due to increased growth of algae in eutrophic condition. In the Principal Component Analysis, the first factor explained the highest percent of the entire variance while the subsequent factors had diminishing variance to explain the water quality. Eigenvalues >1 were taken as criterion for the extraction of the principal components

required for explaining the source of variances in the data set. The PCA revealed three principal components (PC1, PC2 and PC3) with percentage variances of 87.5%, 7.5% and 4.9% respectively. The parameter loadings for the three identified principal components are given in Figure 1, 2, 3. PC1 was positively correlated (loading > 0.75) with dissolved oxygen, BOD, inorganic phosphorous and temperature while negatively correlated with Chlorophyll a, calcium, TS and TSS. PC 2, on the other hand, was positively loaded (loading > 0.75) with chloride, nitrate and TDS while negatively loaded with potassium and pH. PC3 was correlated positively with TSS, calcium, phycobilins and negatively with COD and sodium. These factors appear to be originated from the combined effect of anthropogenic activities such as application of phosphate, sulfate and nitrate fertilizers, and discharge of effluents accompanied with partial ecological recovery system of the river. The first three principal components explained maximum variance, whereas the rest fourteen components accounted for least variance. Based on the strength of the Eigenvalues and the Scree Plots, only the first three principal components were selected for the present study. In the Scree Plot, those points on the vertical limb (steep portion), accounted for the majority of variance, whereas those on the horizontal, flat limb accounted very less for water quality prediction, hence they were ignored (Figure 4). Among different parameters examined, chloride and inorganic phosphorous, indicated by the longest distance from the point of origin in the PCA plot had the most obvious influence on water quality.

The hierarchical clustering produced a dendrogram showing how sampling stations could be clustered and the percentage of replicates where each node is supported was given on the dendrogram after boot strapping. Physico-chemical characteristics of water samples from sampling stations of Vaigai river exhibited 88% similarity between V1 and V3 followed by V2 and V4 with 82% similarity in Bray-Curtis cluster analysis. Nine water quality parameters namely pH, Dissolved oxygen, COD, BOD, alkalinity, chloride, nitrate, TS, TDS were considered for computing WQI and unit weight (Wi) of each parameter was obtained depending upon its weightage. The standard permissible values of various parameters for drinking purpose were considered as recommended by Indian Council of Medical Research (ICMR), World Health Organisation (WHO) and ISI. The permissible limit of WQI for drinking water is 100. The WQI obtained in present study for Vaigai River at individual sampling stations ranged from 114.7 to 195 (Table 2) suggesting the pollution load in Vaigai River and emphasized the need for treating water before supplying for public consumption and propagation of wild life and fish culture. Further, a comprehensive monitoring of water quality for a longer period of time (5 years) can identify the status of the water quality in Vaigai River. The influence of BOD and alkalinity on determination of water quality index was found highest among other seven parameters as reflected by a high  $r^2$  value of 0.924 and 0.911 respectively in regression analysis followed by oxygen ( $r^2 = 0.775$ ) and COD ( $r^2 = 0.523$ ). This is supported by the fact that most cyanobacterial groups found in the selected sampling stations prefer neutral to slightly alkaline pH and in turn increases the BOD of water samples. In membrane filter technique for fecal coliforms, confluent growth of coliforms was observed covering entire filtration area of the membrane and the colonies were not discrete.

Table 1. Correlation coefficient between physico-chemical parameters of Vaigai river samples

	pH	Temp	alk	Cl <sub>2</sub>	O <sub>2</sub>	BOD	COD	TS	TDS	TSS	PO4	NO3	Ca	Na	K	Chloro	Phyco
pH	1																
Temp	0.616	1															
alk	-0.722	-0.110	1														
Cl <sub>2</sub>	-0.819	-0.341	0.390	1													
O <sub>2</sub>	-0.320	0.527	0.744	0.335	1												
BOD	-0.321	0.445	0.840	0.177	0.961	1											
COD	-0.645	-0.451	0.851	0.109	0.313	0.516	1										
TS	-0.377	-0.356	-0.290	0.764	-0.226	-0.443	-0.439	1									
TDS	-0.691	-0.477	0.081	0.937	0.002	-0.174	-0.095	0.927	1								
TSS	0.400	0.038	-0.879	0.084	-0.567	-0.764	-0.907	0.690	0.370	1							
PO4	0.175	0.860	0.408	-0.070	0.876	0.837	0.001	-0.431	-0.352	-0.389	1						
NO3	-0.696	-0.158	0.307	0.978	0.400	0.204	-0.052	0.783	0.912	0.181	0.058	1					
Ca	-0.088	-0.346	-0.597	0.488	-0.519	-0.717	-0.621	0.934	0.749	0.873	-0.588	0.515	1				
Na	-0.821	-0.507	0.903	0.368	0.389	0.535	0.964	-0.209	0.158	-0.828	-0.011	0.212	-0.454	1			
K	0.928	0.279	-0.838	-0.829	-0.643	-0.609	-0.586	-0.277	-0.606	0.484	-0.196	-0.764	0.071	-0.771	1		
Chloro	0.226	-0.353	-0.836	0.082	-0.815	-0.941	-0.671	0.693	0.420	0.910	-0.734	0.095	0.902	-0.610	0.455	1	
Phyco	0.219	0.696	-0.217	0.324	0.437	0.193	-0.696	0.413	0.281	0.483	0.562	0.512	0.331	-0.560	-0.050	0.099	1

Table 2. Water Quality Index of Vaigai river samples

Parameter	Standard value (Si) mg/l (except for pH)	Standards	Wi=K/Si	Water Quality Index			
				V5	V6	V7	V8
pH	7-8.5	ICMR, ISI	0.179	126.4	195	114.7	183.5
DO	5	WHO	0.306				
COD	10	WHO	0.153				
Alkalinity	120	ICMR	0.013				
Chloride	250	WHO, ICMR, ISI	0.006				
BOD	5	ICMR	0.306				
TS	500	ICMR	0.003				
TDS	500	ICMR, ISI, WHO	0.003				
Nitrate	45	ICMR, ISI, WHO	0.034				

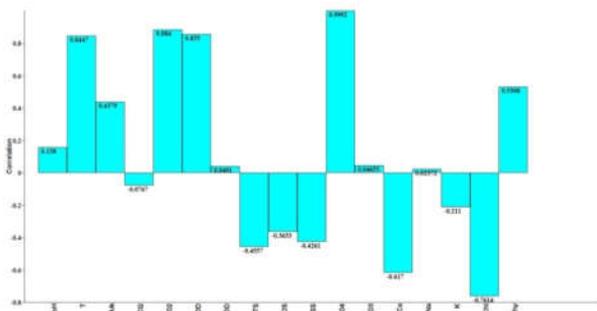


Fig. 1. Loadings chart of principal component-1

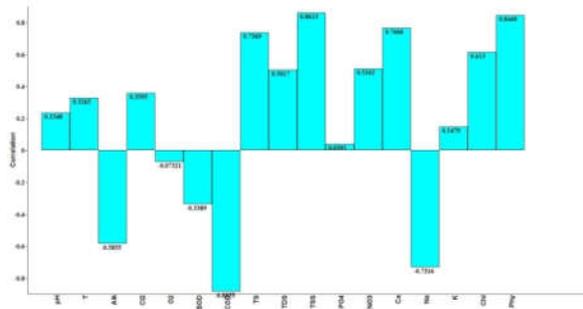


Fig. 3. Loadings chart of principal component-3

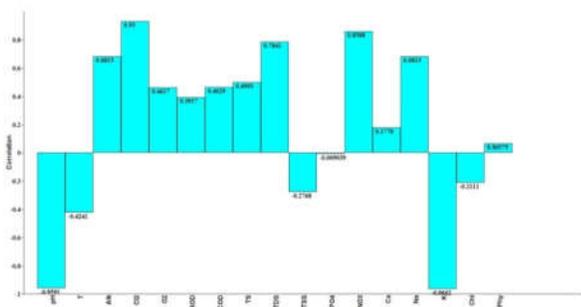


Fig. 2. Loadings chart of principal component-2

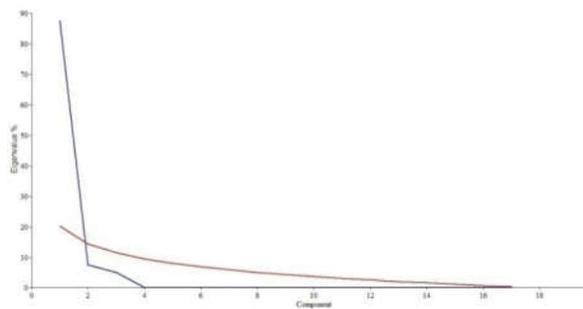


Fig. 4. Scree plot of eigen values of principal components

Most of the sampling sites exhibited highest MPN index (1100/100ml) for fecal streptococcal count with the confidence limit of about 150 to 4800. All the samples throughout the study period showed very high fecal contamination suggesting the poor water quality.

Microscopic observation of the samples revealed the presence of diverse forms of cyanobacteria with most belonged to the order Nostocales. Vaigai River samples were composed of the morphologically different genera *Anabaena*, *Nostoc*, *Rivularia*, *Spirulina* of the order Nostocales; *Oscillatoria*, *Leptolyngbya* and *Phormidium* of the Oscillatoriales; *Synechocystis*, *Chroococciopsis*, *Chroococcus*,

*Merismopedia* of the Chroococcales. This observation is supported by the observation of Desikachary (1959), who reported these cyanobacteria in Shembaganur, Madurai district. Water samples from sampling stations of Vaigai River were screened for the presence of microcystin and compared with standard microcystin LR calibrators (C1, C2 and C3). In photometric analysis, % B0 of the calibrators was compared graphically on a log scale with the % B0 of the water samples. Microcystin concentration of Vaigai river site 4 (1 µg/l) reached the WHO maximum permissible limit of microcystin for consumption (1 µg/l). Vaigai river site 1 showed microcystin concentration of 0.94 µg/l followed by Vaigai river site 3 with 0.8 µg/l. Vaigai river site 2 was found to have microcystin concentration of 0.7 µg/l which exceeds the concentration of standard microcystin LR calibrator C2 (above 0.64 µg/l). Availability of excessive phosphorous into the watershed due to washing activities supported the luxurious growth of toxic cyanobacteria and resulted in tremendous increase of toxin concentration. This study clearly indicates that the Vaigai river in Madurai city of South India is already existing below the standards of the drinking water quality and for human consumption. This method of water quality assessment can be introduced in all the urbanized area for effective water quality management.

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