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Assessment of seasonal variations in water quality of Brahmani river using PCA

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Abstract. Assessment of seasonal changes in surface water quality is an important aspect for evaluating temporal variations of river pollution due to natural or anthropogenic inputs of point and non-point sources. In this study, surface water quality data for 15 physico-chemical parameters collected from 7 monitoring stations in a river during the years from 2014 to 2016 were analyzed. The principal component analysis technique was employed to evaluate the seasonal correlations of water quality parameters, while the principal factor analysis technique was used to extract the parameters that are most important in assessing seasonal variations of river water quality. Analysis shows that a parameter that is most important in contributing to water quality variation for one season may not be important for another season except alkalinity, which is always the most important parameters in contributing to water quality variations for all three seasons.

Keywords: principal component analysis; seasonal variation; surface water quality

1. Introduction

Water is the most important natural resource not only of a state or a country, but of the entire humanity. The prosperity of a nation depends primarily upon the judicious exploitation of this resource. Thus, it can be stated that the primary wealth of a nation is water, which flows in rivers and streams. The available fresh water to man is hardly 0.3-0.5% of the total water available on the earth and therefore, its judicious use is imperative (Hegde and Kale 1995). Water is an essential requirement of human and industrial developments and it is one the most delicate part of the environment (Das and Acharya 2003). Rapid increase of industrialization, urbanization, and population increase in the last few decades have caused a dramatic increase in the demand for river water, as well as significant deteriorations in water quality throughout the world (Ahmad *et al.* 2010, Bakali *et al.* 2014, Canfield *et al.* 1984, Chun *et al.* 1999, Dassenakis *et al.* 1998, Facetti *et al.* 1998, Satter and Islam 2005, Zakir *et al.* 2013).

The Brahmani River is one of the major lifelines in the state of Odisha in Eastern India. It is formed by the confluence of the Sankh and South Koel rivers, near Rourkela at 22°15’N and 84°

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Table 1 Test methods for various parameters of water samples

Parameters	Methods adopted
pH	Systronic-361 pH meter
Temperature	Thermometer
DO (mg/l)	Winkler's method
Electrical Conductivity(EC)	Systronic-Conductivity meter
TDS (mg/l)	Water analysis kit model 191 E
Alkalinity (mg/l)	Titration
Sodium, Magnesium, Calcium, Potassium ion (mg/l)	Flame Photometry
Chloride (Cl^-) (mg/l)	Titrating against N/50 solution of silver nitrate using potassium chromate as indicator
Fluoride (F^-) (mg/l)	Orion Ion specific electrode using the standard procedure recommended by APHA (1995)
Sulfate(SO_4^{2-}), Nitrate (NO_3^-) Phosphate (PO_4^{3-})(mg/l)	Spectrophotometrically using the standard procedure recommended by APHA (1995)

2.1 Study area

Fig. 1(a) and Fig. 1(b) show the Brahmani River Basin and sampling stations along the river. The River basin has a total drainage area of 39,268 km^2, out of which 22,516 km^2 is in Odisha state, 15,405 km^2 in Jharkhand state and 1,347 km^2 in Chhattisgarh state. The river referred as Brahmani River at the confluence point near Vedvyas, in Odisha at an elevation of 200 m above mean sea level. The land uses within the basin largely consist of residential, commercial, industrial, mining, livestock, pasture, row crops, forestry, and water. The sampling sites selected from upstream(U/S) to downstream(D/S) are as follows: Panposh D/S, Rourkela D/S, Rengali, Talcher U/S, Kamalanga D/S, Bhuban, Pattamundai.

2.2 Methodology of sampling and analysis

In order to classify surface water quality at major locations of the river, a number of water samples were collected from seven locations which are shown in Fig. 1(b). Water samples were collected at a distance of approx. 0.5 meter below the water surface, monthly for three years i.e., 2014, 2015 and 2016. Water samples from different sampling stations are collected in standardized PET (polyethylene terephthalate) bottles having 1.5 litre capacities with stopper. The bottles were washed thoroughly with 2% nitric acid and subsequently rinsed with distilled water. The bottles were then preserved in a clean place. Before taking the water samples, all the supply bottles are rinsed with sample water 2-3 times. As all the physicochemical parameters are measured within 24 hours of sample collection, there is very little possibility of changing concentration of any parameters. The sampled bottle is made watertight by air tightening it inside water. Precautions have been taken to remove any air bubble present. Each container was clearly marked with the name and date of sampling. Fifteen physicochemical parameter namely pH, Temperature, DO, TDS, EC, Alkalinity, Na^+, Ca^{2+}, Mg^{2+}, K^+, F^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} have been taken for analysis. These physico-chemical parameters selected for the study contribute to the change in river water quality. The methodologies adopted for determination of water quality parameters of

These data imply that the ions have more influence on TDS than EC. Therefore, seasonal variations should be considered when using TDS or EC as an indicator to evaluate surface water quality. Sodium ions are well known for raising conductivity and decreasing soil permeability. In summer, Na^+ had high positive correlation with Cl^- (0.92) and had a moderate positive relation with Ca^{2+} (0.696), K^+ (0.748), F^- (0.72), NO_3^- (0.645) and SO_4^{2-} (0.767). In monsoon, correlation between Na^+ and Cl^- is seen very strong (0.98) and Na^+ had a moderate positive correlation with Ca^{2+}, F^-, NO_3^-, SO_4^{2-} (0.58-0.71) in winter (Table 2). The high correlation in monsoon compared to summer and winter may be due to leaching of minerals (e.g., gallite, sylvite) from rocks, saline deposits and surface runoff entering into the river.

3.2 Temporal variations of water quality parameters

In PCA, eigen values are normally used to determine the number of principal components (PCs) that can be retained for further study. A scree plot for the eigen values obtained in this study shows a pronounced change of slope after the third eigen value in summer and winter whereas in monsoon scree plot change of plot is observed after fifth eigen value (Fig. 2). Therefore, the first three PCs of summer and winter and first five PCs of monsoon will be used for further analysis. These three PCs have eigen values greater than or close to unity for summer and winter, explain 73.70% and 70.32% of the total variances of information contained in the original data set respectively. For monsoon, the five PCs have eigen value greater than or close to unity and explain 74.81% of the total variance.

Projections of the original variables on the subspace of the PCs are called component loadings and coincided with the correlation coefficients between PCs and variables. In other words, the component loadings are the linear combinations for each principal component, and express the correlation between the original variables and the newly formed components. The component loadings can be used to determine the relative importance of a variable (or parameter in this study) as compared to other variables in a PC and don’t reflect the importance of the component itself.

Component loadings of the first two retained PCs for each season are presented in Fig. 3. In summer, the principal component (PC1) explained 54.6% of the total variance and was positively and largely contributed by major cations (i.e., Na^+, Ca^{2+}, $Mg^{2+}$and K^+), major anions (i.e., F^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) , TDS, alkalinity and EC and was negatively affected by pH, Temperature and DO. Therefore, this component seems to measure the dominance of major cations, major anions, TDS and EC over the pH, Temperature and DO (Singh *et al.* 2005). This component reveals that all the selected physicochemical parameters were important in accounting for river water quality variations in summer since the loading (eigenvector) coefficients are high.PC2 explained 10.5% of total variance and was positively and largely contributed by water temperature, DO, NO_3^- and PO_4^{3-} and negatively due to pH, alkalinity, Ca^{2+} and Mg^{2+} (Fig. 3). This component distinguishes the importance of water temperature, DO, NO_3^- and PO_4^{3-} over alkalinity, Ca^{2+} and Mg^{2+}.

Similar component loading patterns are obtained for PC1 in monsoon except for PO_4^{3-} (Fig. 3). That is, PC1 (which explained 34.1% of the total variance) was positively contributed by TDS, alkalinity, EC, major cations (i.e., Na^+, Ca^{2+}, $Mg^{2+}$and K^+) and major anions (i.e., F^-, Cl^-, NO_3^- and SO_4^{2-}) and was negatively affected by pH, DO and PO_4^{3-}. This component also reveals that the pH was less important in accounting for river water quality variations in monsoon since the loading (eigenvector) coefficient were low for the parameter. The PC2 (which explained 12.8% of the total variance) was positively contributed by pH, alkalinity, Ca^{2+}, Mg^{2+} and F^- and was

Table 2 Continued

Alkal	0.027	-0.196	-0.037	0.669	1										
EC	-0.273	-0.188	-0.285	0.98	0.623	1									
Na^+	-0.209	-0.082	-0.236	0.86	0.49	0.838	1								
Ca^{2+}	-0.134	-0.139	-0.262	0.903	0.714	0.879	0.691	1							
Mg^{2+}	-0.14	-0.234	-0.193	0.674	0.69	0.658	0.463	0.593	1						
K^+	-0.232	-0.048	-0.311	0.728	0.3	0.722	0.808	0.546	0.452	1					
F^-	-0.303	-0.186	-0.301	0.769	0.322	0.776	0.717	0.653	0.416	0.721	1				
Cl^-	-0.221	-0.063	-0.201	0.826	0.473	0.803	0.978	0.638	0.44	0.819	0.679	1			
NO_3^-	-0.227	-0.122	-0.277	0.613	0.218	0.594	0.592	0.515	0.277	0.665	0.714	0.548	1		
SO_4^{2-}	-0.319	-0.176	-0.316	0.81	0.296	0.827	0.589	0.738	0.511	0.552	0.752	0.531	0.518	1	
PO_4^{3-}	0.057	-0.216	-0.172	-0.033	-0.095	-0.02	-0.084	-0.061	-0.056	-0.004	0.04	-0.077	0.061	0.01	1

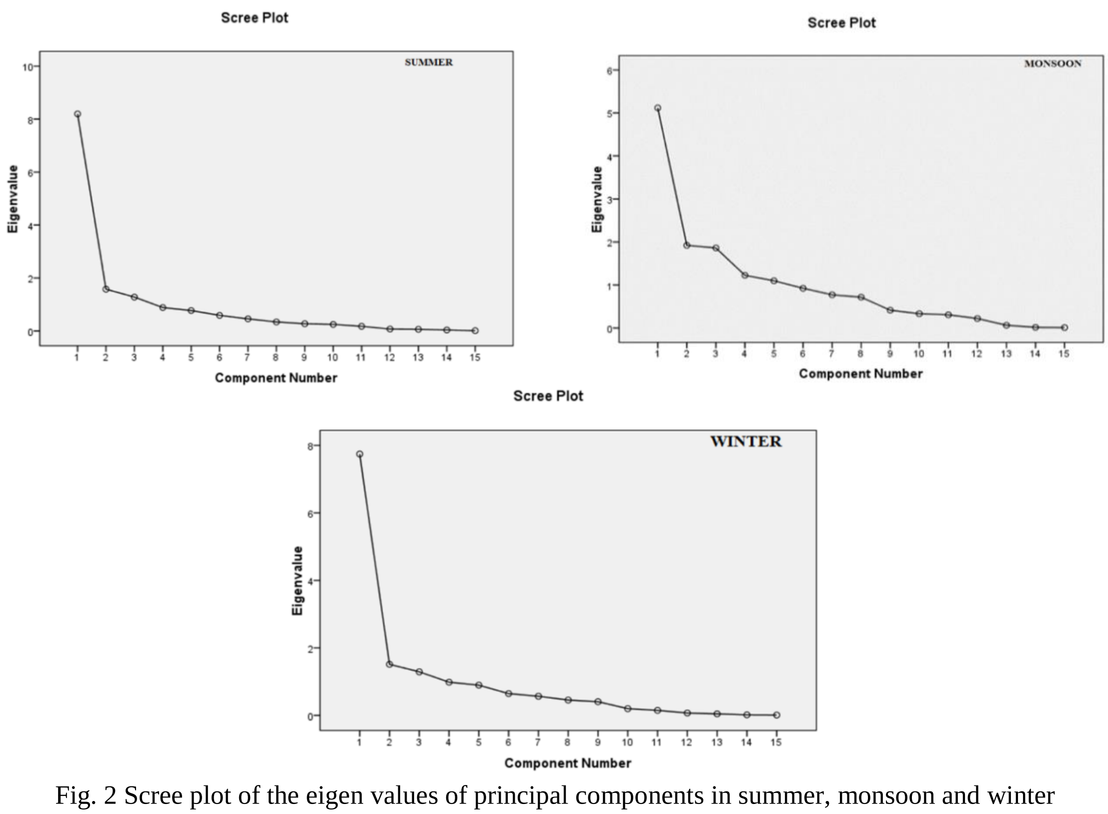

Fig. 2 Scree plot of the eigen values of principal components in summer, monsoon and winter

negatively impacted by Na^+, Cl^- and PO_4^{3-}.

In winter, the PC1, which accounted for 51.6% of the total variance, was positively and largely influenced by TDS, alkalinity, EC, major cations (i.e., Na^+, Ca^{2+}, $Mg^{2+}$and K^+) and major anions (i.e., F^-, Cl^-, NO_3^- andSO_4^{2-}) and was negatively affected by pH and DO as indicated in Fig. 3. This component also demonstrates that water temperature and PO_4^{3-} were less important in accounting for river water quality variations in winter since the loading (eigenvector) coefficients were low

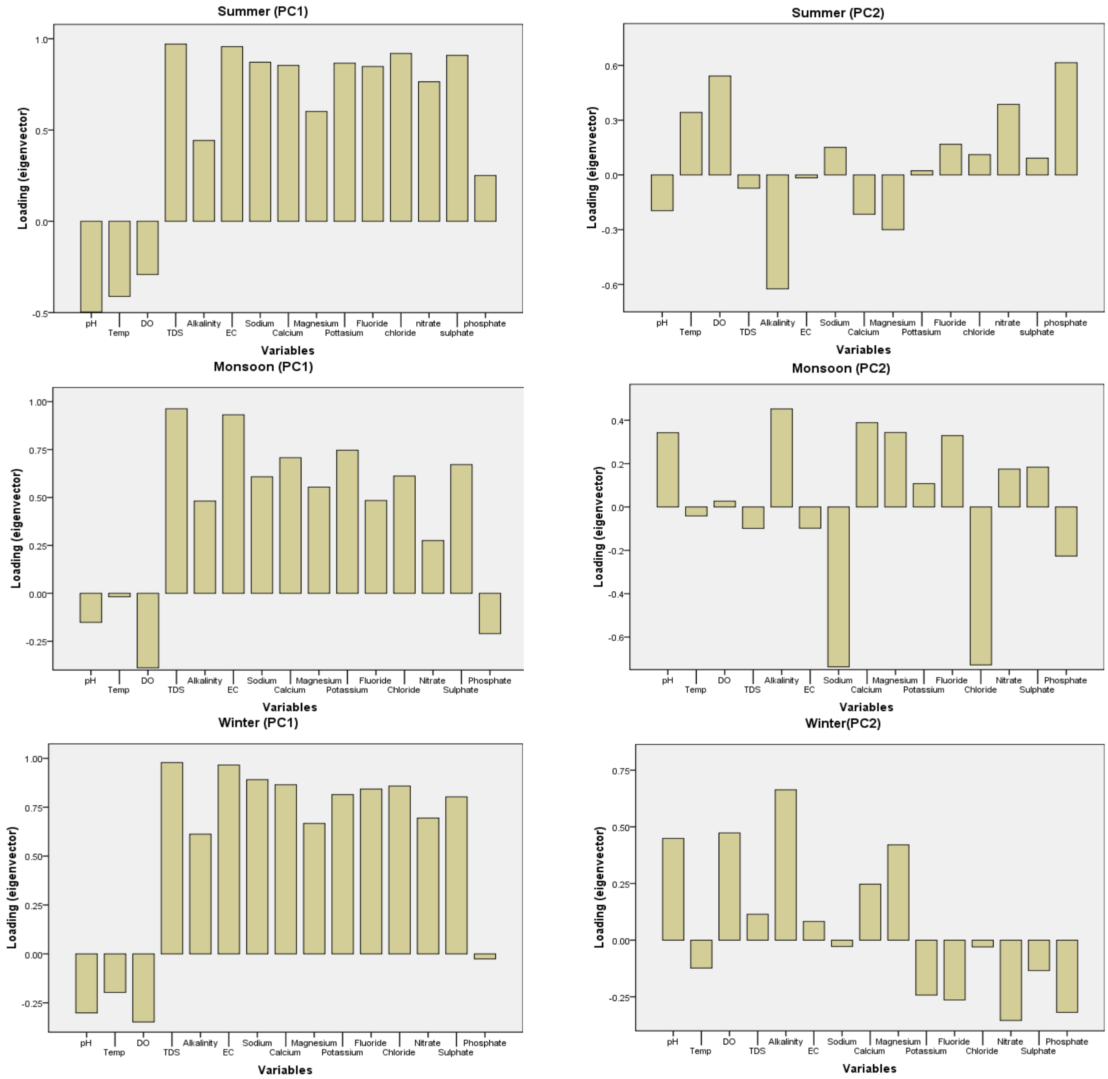

Fig. 3 Component loadings for the first component (PC1) and the second component (PC2) in summer, monsoon and winter

Table 3 Rotated factor correlation coefficients for each season

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
			Summer		
SO_4^{2-}	0.892	0.217	-0.153		
Cl^-	0.859	0.349	0.009		
NO_3^-	0.855	0.019	0.115		
F^-	0.836	0.225	-0.007		
EC	0.833	0.478	-0.046		
K^+	0.826	0.245	-0.193		
Na^+	0.823	0.324	0.064		

Table 4 Most important water quality parameter in each season

Season	Positively correlated parameter	Negatively correlated parameter
Summer	TDS, EC, Alkal, K^+, Na^+, Cl^-,F^-, NO_3^{2-}, SO_4^{2-}	-
Monsoon	Alkal, Na^+, Cl^-, NO_3^{2-}, T, Mg^{2+}	-
Winter	Alkal, TDS, EC, Ca^{2+}	-
These parameters were selected with factor correlation coefficients greater than 80%		

water quality variation for one season may not be important for another season. Therefore, when selecting water quality parameters for the establishment of pollutant load reduction goals (PLRGs) and the development of total maximum daily loads (TMDLs), the seasonal water quality parameter variations must be considered.

4. Conclusions

• In this study, surface water quality data for 15 physico-chemical parameters collected from seven monitoring stations along the main stem of the Brahmani River, Odisha from 2014 to 2016 were analysed, using the PCA and PFA techniques. Results from PCA show that river water temperature, pH and DO had a relatively weak correlation with other water quality parameters for the entire three seasons.

• Strong correlations between TDS, EC and the Na^+, Ca^{2+}, K^+, F^-, Cl^-, NO_3^- and SO_4^{2-} were found in summer (>0.70), but the correlation were reduced sharply in monsoon (<0.6), and finally recovered in winter (0.60-0.90). The results indicate that TDS, EC was not always highly correlated to Na^+, Ca^{2+}, K^+, F^-, Cl^-, NO_3^- and SO_4^{2-}. Therefore, seasonal variations should be considered when using TDS and EC as an indicator parameter to evaluate surface water quality in the Brahmani River.

• Strong correlation is observed between Na^+ and Cl^- (>0.92) for the entire three seasons. Such high correlation may be attributed to discharge of domestic and industrial waste water to the river Brahmani.

• Result from the PFA show that a parameter that is important in contribution to river water quality variation for one season may not be important for another season. Therefore, when selecting water quality parameters for the establishment of pollutant load reduction goals (PLRGs) and the development of total maximum daily loads (TMDLs), the seasonal variation of parameters on river water quality must be considered.

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