

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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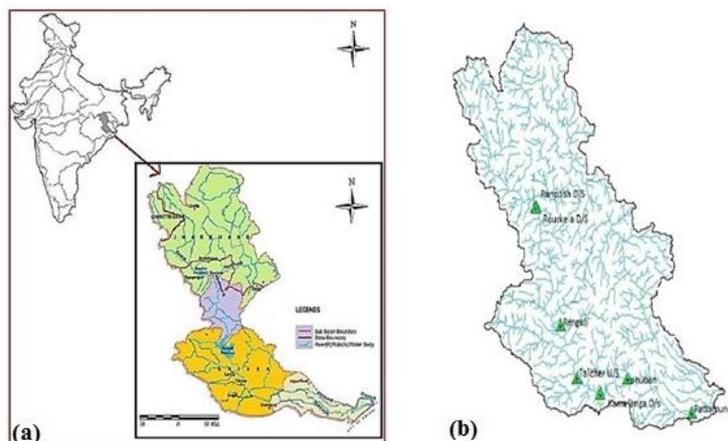


Fig. 1(a) Study area showing the Brahmani River Basin, (b) Brahmani River Basin along with seven sampling stations (Symbol “ Δ ” represents the surface water-monitoring stations)

47°E and flows through the different districts of the state such as Sundergarh, Kendujhar, Dhenkanal, Cuttack and Jajpur and finally falls in Bay of Bengal. People living on the bank of the river primarily use the water for drinking purposes in addition to industrial, agricultural and other purposes. The wastewater from point and non-point sources such as industrial, agricultural and sewage systems is generally discharged into the river throughout its stretch. In addition, run off from the rural settlements (Devi *et al.* 2013, Gupta *et al.* 2009, Jain 2004, Shikazono *et al.* 2012, Zakir *et al.* 2016), open defecations, dumping of carcasses and disposal of dead bodies (Moingt *et al.* 2013) also contribute to increasing degree of pollution (Islam *et al.* 2015, Mohiuddin *et al.* 2011, Mohiuddin *et al.* 2012, Shikazono *et al.* 2012, Zakir *et al.* 2017). In view of this, evaluations of river water quality to find its suitability for various usages along the stretch of river and in different seasons is utmost necessary to abate the population sufferings from diseases and ill health. Characterization 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 addition, pollutants entering a river system normally result from many transport pathways including storm water runoff, discharge from ditches and creeks, groundwater seepage, and atmospheric deposition. These pathways are seasonal-dependent (Rahman *et al.* 2012). In recent years, the principal component analysis (PCA) and principal factor analysis (PFA) techniques have been applied to a variety of environmental applications, including evaluation of ground water monitoring wells and hydrographs, examination of spatial and temporal patterns of surface water quality, identification of chemical species related to hydrological conditions, and assessment of environmental quality indicators (Bengraïne and Marhaba 2003, Gangopadhyay *et al.* 2001, Ouyang 2005, Perkins and Underwood 2000, Shine *et al.* 1995, Tauler *et al.* 2000, Vega *et al.* 1998, Voutsas *et al.* 2001, Yu *et al.* 1998). The aim of this study is to apply PCA and PFA techniques to evaluate the seasonal correlations of water quality parameters of Brahmani river and to extract those parameters that are most important in assessing seasonal variations of the river water quality.

2. Materials and methodology

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 km², out of which 22,516 km² is in Odisha state, 15,405 km² in Jharkhand state and 1,347 km² 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⁺, Ca²⁺, Mg²⁺, K⁺, F⁻, Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻ 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

the collected samples are shown in Table 1.

2.3 PCA and PFA analysis

The PCA and PFA were performed on SPSS (Statistical Package for the Social Sciences) software, version 16, developed SPSS Inc. In mathematical terms, PCA and PFA involve the following five major steps: (1) start by coding the variables x_1, x_2, \dots, x_p to have zero means and unit variance, i.e., standardization of the measurements to ensure that they all have equal weight in the analysis; (2) calculate the covariance matrix C ; (3) find the eigen values $\lambda_1, \lambda_2, \dots, \lambda_p$ and the corresponding eigenvectors a_1, a_2, \dots, a_p ; (4) discard any components that only account for a small proportion of the variation in datasets; and (5) develop the factor loading matrix and perform a varimax rotation on the factor loading matrix to infer the principal parameters. In this study, only those components or factors exhibiting an eigen value of greater than or close equal to one were retained (Voutsas *et al.* 2001, Bengraïne and Marhaba 2003).

In order to distinguish the variations of each parameter for a given season, the data was divided into three distinct temporal databases. Winter corresponded from October to February, summer from March to June, and monsoon from June to September. Therefore, three seasonal separation principal components or factors were performed.

3. Results and discussion

3.1 Seasonal correlation of water quality parameters

Table 2 provides the seasonal correlation matrix of the water quality parameters obtained from the PCA. In general pH, water temperature, DO, and PO_4^{3-} had relatively weak correlations, i.e., most of the correlation coefficients are less than 0.7 (absolute value) with other parameters for entire three seasons. In summer, the correlation coefficients between pH and other parameters were less than or equal to 0.21 which signifies weak relationship except for sulphate showing negative increase in correlation (-0.54). The negative increase in correlation with sulphate shows that water is alkaline in nature (Singh *et al.* 2005).

Table 2 reveals that TDS has a strong positive correlation with EC (0.96), Na^+ (0.84), Ca^{2+} (0.89), K^+ (0.82), Cl^- (0.88), SO_4^{2-} (0.86) and moderate positive correlation with alkalinity (0.55), Mg^+ (0.57), F^- (0.76), and NO_3^- (0.70) in summer season. Similar correlation were found in winter season where TDS has strong positive correlation with EC (0.98), Na^+ (0.86), Ca^{2+} (0.90), Cl^- (0.82), and SO_4^{2-} (0.81) and moderate positive correlation with alkalinity (0.66), Mg^{2+} (0.67), K^+ (0.72), F^- (0.76) and NO_3^- (0.61). This indicates that these ions contribute major part to the TDS of the water. In monsoon season, TDS shows strong positive correlation with EC (0.97) and moderate positive correlations with Na^+ (0.64), Ca^{2+} (0.67), K^+ (0.62), Cl^- (0.65) and SO_4^{2-} (0.61). Alkalinity shows moderate positive correlation with Ca^{2+} (0.62) and Mg^{2+} (0.53) in summer, with EC (0.50) and Ca^{2+} (0.53) in monsoon and with EC (0.62), Ca^{2+} (0.71) and Mg^{2+} (0.69) in winter (Table 2). In summer, EC has significant positive correlation with the Na^+ (0.84), Ca^{2+} (0.86), Cl^- (0.88), SO_4^{2-} (0.88) and moderate positive correlation with Mg^+ (0.55), K^+ (0.78), F^- (0.76) and NO_3^- (0.69), but the correlations were moderately reduced in monsoon, and finally recovered in winter. That is correlation coefficient between EC and Na^+ , Ca^{2+} , Mg^{2+} , K^+ , F^- , Cl^- , NO_3^- , SO_4^{2-} were in the range of 0.21-0.64 in monsoon and 0.59-0.87 in winter.

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	

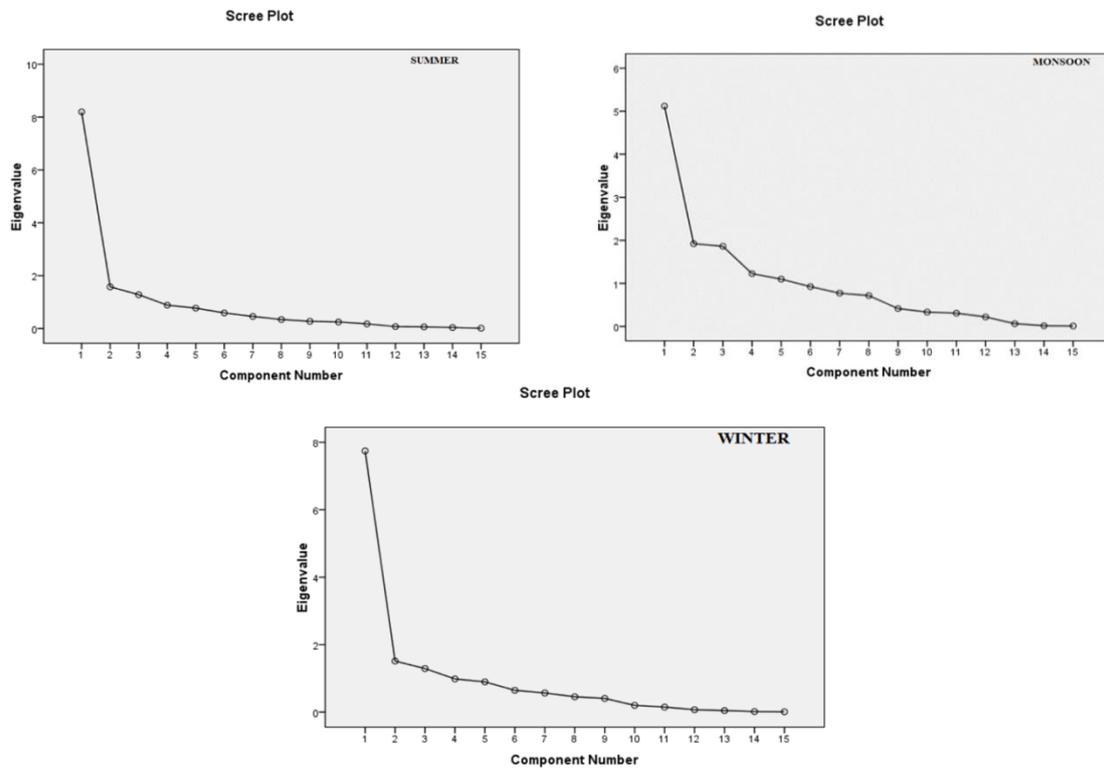


Fig. 2 Scree plot of the eigen values of principal components in summer, monsoon and winter

negatively impacted by Na⁺, Cl⁻ and PO₄³⁻.

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⁺, Ca²⁺, Mg²⁺ and K⁺) and major anions (i.e., F⁻, Cl⁻, NO₃⁻ and SO₄²⁻) and was negatively affected by pH and DO as indicated in Fig. 3. This component also demonstrates that water temperature and PO₄³⁻ were less important in accounting for river water quality variations in winter since the loading (eigenvector) coefficients were low

for these two parameters. PC2 explained 10.09% of the total variance and was positively influenced by pH, DO, alkalinity, Ca^{2+} and Mg^{2+} and was negatively influenced by K^+ , F^- , SO_4^{2-} , NO_3^- and PO_4^{3-} (Fig. 3). This component distinguishes the importance of pH, DO, alkalinity, Ca^{2+} and Mg^{2+} over K^+ , F^- , NO_3^- and PO_4^{3-} (Singh *et al.* 2005).

Vega *et al.* (1998) investigated the seasonal and polluting effects on water quality of the Pisuerga River (Duero basin, Spain) using exploratory data analysis. These authors reported that the overall component loadings (i.e., no seasonal loading provided) for 22 experimental variables used in their study were 46.1% and 19.0% respectively for PC1 and PC2. These values were lower than those from our study for PC1. In addition, the PC1 in their study was mostly contributed by chloride, bicarbonate, sulfate, conductivity, dissolved solids, hardness, calcium, potassium, magnesium, and sodium, whereas the PC1 in our study was largely 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-}). We attributed the discrepancies to the different river environments and different water quality parameters as well as to the different time periods (i.e., seasonal) used in each study.

Results suggested that water quality variables that play important roles in influencing river water quality in one environment may not be important in another environment.

3.3 Identification of important seasonal water quality parameter

Fig. 3 shows the component loadings for the first component (PC1) and the second component (PC2) for all the seasons. PC1 and PC2 for all the seasons were highly influenced (negatively or positively) by most of the variables, thus hindering the interpretation regarding which parameters are more important than the others in influencing water quality variations within a given season. Therefore, the PFA is needed to circumvent the ambiguity in the data.

Table 3 shows the rotated correlation coefficients for the first three factors in summer and winter whereas five factor in monsoon season. The reason to retain the first three factors in summer and winter for analysis is that these three factors account for 73.70% and 70.32% of the total variances in summer and winter, respectively. For monsoon, five factors account for 74.81% of the total variances. The rest of the factors accounted for only small percentages of the total variances and had very low and insignificant correlation coefficients. By one rule of thumb in confirmatory factor analysis, loadings should be 0.7 or higher to make it confirm that independent variables identified a priori were represented by a particular factor, on that rationale the 0.7 was corresponded to about half of the variance in the indicator were being explained by the factor. In this study, any water quality parameter with an absolute correlation coefficient value $>80\%$ (0.8) was considered to be an important parameter contributing to seasonal variations of the Brahmani River water quality.

The most important water quality parameters that may be used to evaluate seasonal variations of the Brahmani River water quality are given in Table 4. The parameters have been identified based on 80% selection criterion. The parameters such as TDS, EC, Alkal, K^+ , Na^+ , Cl^- , F^- , NO_3^- and SO_4^{2-} are identified as the most important parameters and positively contributed to water quality variations in summer (Table 4). In monsoon, Alkali, Na^+ , Cl^- , SO_4^{2-} , T and Mg^{2+} are identified as most important parameters and positively contributed to water quality variations. During winter, the parameters like Alkali, TDS, EC and Ca^{2+} are positively correlated. Table 4 further reveals that alkalinity is always the most important variables contributing to water quality variations in Brahmani River for all three seasons.

This study demonstrated that a water quality parameter that is important in contribution to

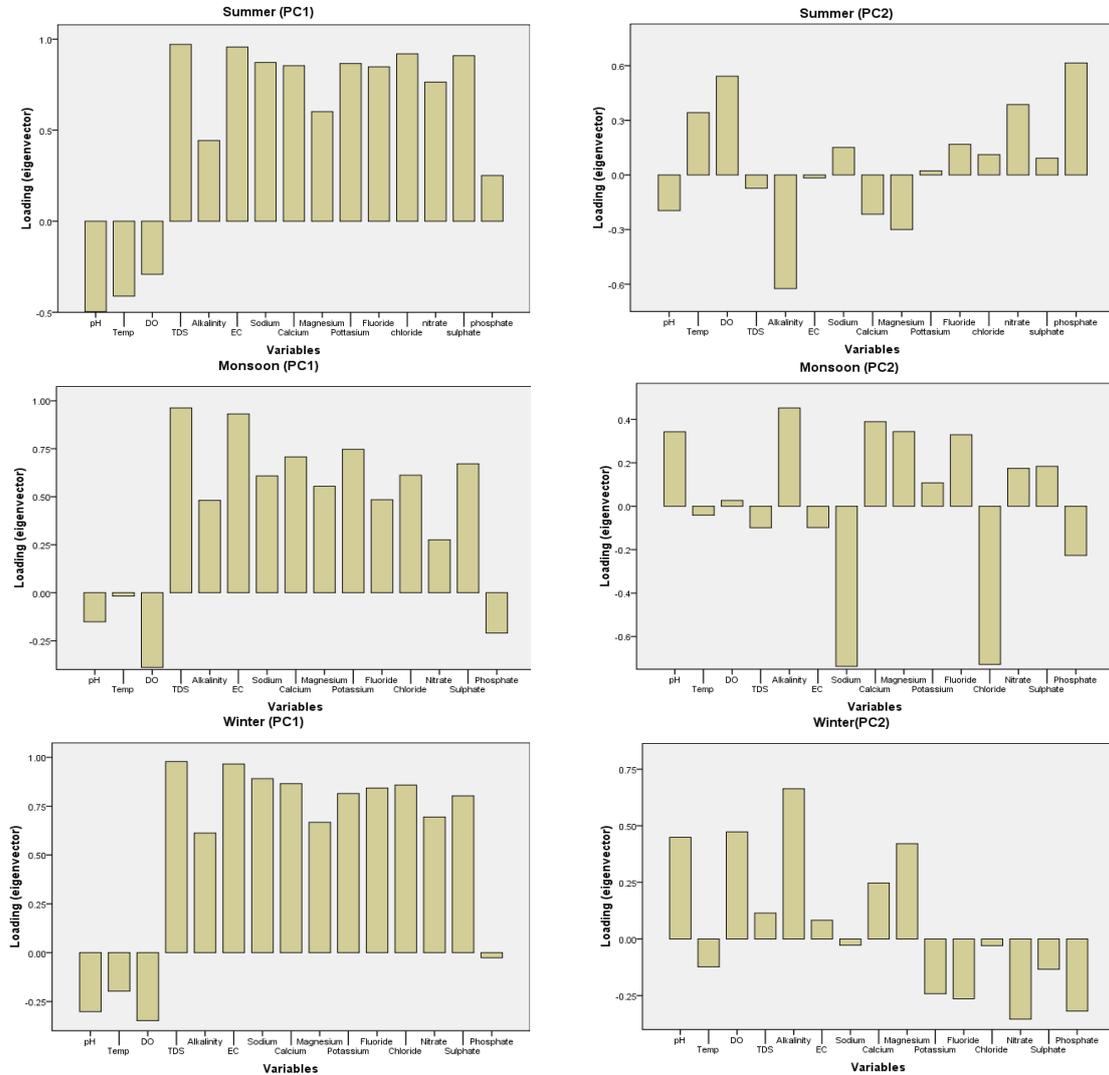


Fig. 3 Component loadings for the first component (PC1) and the second component (PC2) in summer, monsoon and winter

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 3 Continued

TDS	0.814	0.549	-0.054		
pH	-0.652	0.283	0.321		
Ca ²⁺	0.642	0.624	-0.101		
Alkal	0.039	0.929	-0.093		
Mg ²⁺	0.384	0.569	-0.133		
DO	-0.178	-0.126	0.766		
PO ₄ ³⁻	0.347	0.03	0.727		
T	-0.281	-0.279	0.396		
Monsoon					
Cl ⁻	0.984	0.044	0.028	0.085	-0.017
Na ⁺	0.981	0.07	0.021	0.04	-0.04
Alkal	-0.037	0.832	-0.241	0.299	0.007
Ca ²⁺	0.04	0.732	0.363	0.231	0.052
EC	0.581	0.665	0.329	0.175	0.021
TDS	0.609	0.62	0.365	0.25	0.01
NO ₃ ⁻	-0.145	0.009	0.832	-0.078	-0.111
SO ₄ ²⁻	0.151	0.202	0.788	0.311	-0.031
K ⁺	0.262	0.427	0.625	0.191	0.111
pH	-0.249	0.137	-0.463	0.314	0.048
Mg ²⁺	0.161	0.224	0.084	0.828	0.108
PO ₄ ³⁻	-0.061	-0.048	0.192	-0.612	0.349
F ⁻	0.043	0.223	0.292	0.544	0.002
T	0.033	0.146	-0.092	-0.137	0.826
DO	-0.166	-0.538	-0.057	0.22	0.618
Winter					
Alkal	0.899	-0.136	-0.029		
TDS	0.832	0.527	0.004		
Ca ²⁺	0.83	0.351	-0.011		
EC	0.804	0.543	-0.009		
Mg ²⁺	0.798	0.078	-0.153		
Na ⁺	0.655	0.603	0.233		
Cl ⁻	0.627	0.587	0.259		
F ⁻	0.491	0.733	-0.043		
K ⁺	0.465	0.717	0.167		
NO ₃ ⁻	0.315	0.714	-0.009		
SO ₄ ²⁻	0.549	0.599	-0.127		
DO	0.01	-0.568	0.243		
pH	0.045	-0.535	0.064		
PO ₄ ³⁻	-0.163	0.169	-0.732		
T	-0.289	0.034	0.71		

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⁺, Ca²⁺, K⁺, F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ 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⁺, Ca²⁺, K⁺, F⁻, Cl⁻, NO₃⁻ and SO₄²⁻. 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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