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MULTIVARIATE STATISTICAL ANALYSIS OF POLLUTANTS IN ENNORE CREEK, SOUTH-EAST COAST OF INDIA

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ABSTRACT

Multivariate statistical techniques involving factor analysis (FA) and dendrograms for hierarchical cluster analysis (HCA) were performed on nine water samples from Ennore Creek, Chennai, Tamil Nadu to assess the spatial distribution of water quality in each of three seasons. The water samples were analyzed for distribution of physicochemical parameters such as WT, pH, Salinity, DO, BOD, TSS, NO_2^-, NO_3^-, NH_4^+, TN, IP and TP**.** Results of factor analysis clearly indicates that factor 1 is dominant in monsoon season, since the estuarine mouth is partially opened (50-75m wide). When compared to pre and post-monsoon, maximum enrichment of nutrients occurs during the monsoon season. It is attributed due to the constricted outlet of the creek and large scale inflow of pollutants due to precipitation. Further the factor analysis indicates that the parameters responsible for water quality variations are mainly related to the influence of municipal sewage, agricultural effluents and industrial waste water. With HC analysis the water samples have classified into 3 clusters during the pre-monsoon season, monsoon season and post-monsoon season. pre-monsoon cluster II, monsoon cluster III and post-monsoon cluster III are having highest concentration in WT, BOD, NO_3^-, NH_4^+, TN, IP and TP. The characteristics and water quality of these cluster stations EBUCS, WQE4 and WQE5 are in direct relation with Buckingham canal source and NCTPS coolant water.

Keywords: Physico-chemical; Multivariate statistics; Ennore Creek; Nutrient cycles

1. Introduction

High degree of industrialization and urbanization has led to a strong risk of heavy metal contamination in the coastal ecosystems in tropical and subtropical countries. It can also affect the function of heavy metal contaminants in soil and sediment. Evaluating the impacts of land use change is important to protect ecosystem resources (Charlesworth and Foster, 1999). Estuarine and coastal sediments are generally considered as a sink for metals and metalloids (Yao *et al.*, 2007). Various studies have demonstrated sediments from coastal areas greatly contaminated by heavy metals, therefore, the evaluation of metal distribution in surface sediments is useful to assess pollution in the marine environment (Muthuraj and Jeyaprakash, 2007). In estuarine regions, larger amounts of contaminated suspended sediments begin to flocculate and settle at the bottom due to the hydrodynamic setting of minor river basins with distinctive sedimentary patterns, which are formed due to changes in salinity, water temperature and redox effects (Gijs *et al.*, 2002). Eutrophication is of great environmental distress, leading to complicity in the aquatic environment, causing problems such as formation of algal blooms which results reduction in oxygen levels, leads to mortality of aquatic fauna and flora and eventually loss of biodiversity (Yadav *et al.*, 2007). India is bestowed with long coastline of 8,129 km and of this 6,000 km is rich in estuaries, creeks, brackish water, lagoons and lakes. The southeast coast of India is an important stretch of coastline, where many major rivers drain into the Bay of Bengal and they are also richer in marine fauna and flora.

The application of different multivariate statistical techniques, such as cluster analysis (CA), Factor analysis and correlation analysis, helps in the interpretation of complex data matrices to better understand the water quality and ecological status of the study area. Also, these techniques allow the identification of possible factors/sources that influence water systems and offer valuable tools for reliable management of water resources as well as rapid solution to pollution problems (Simeonoya *et al.*, 2003; Wunderlin *et al.*, 2001). The aim of present research is to study the seasonal and special nutrient variation and change in physicochemical parameter due to the impact of pollution sources and discharge of untreated sewage into Ennore Creek environment.

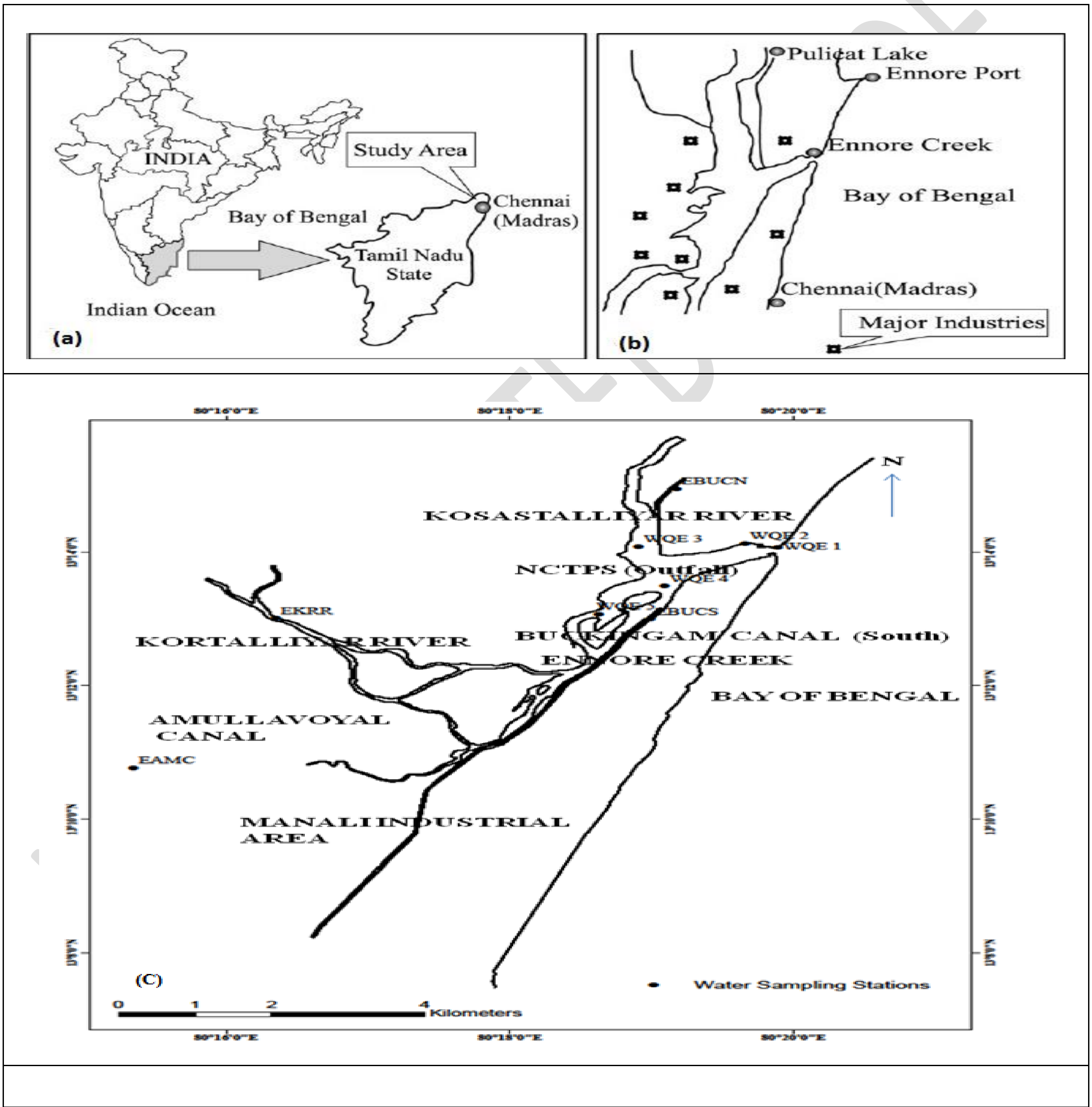

Figure1 (a-c). Map showing the study area with sampling locations and its environs

2. Material and Methods

2.1. Study area description

The Ennore Creek is located at Latitude 13°14’10”N and Longitude 80°19’00”E on the south east coast of India about 20 kilometers North of Chennai (Fig 1 a & b). The total area of the creek is 4 Km^2 and is nearly 400m wide. Creek is connected to the Pulicat Lake in the North and to the Kortalliyar River in the South. The Northern side of the Ennore Creek is the Kosasthalaiyar backwater which is connected to the Pulicat Lake, North Chennai Thermal power Station and the Ennore Port. The Southern side of the Ennore Creek is bounded by Kortalliyar River and Amullavoyal Canal. The Buckingham canal traversing through the Ennore creek enters Ennore near the Railway Bridge and receives urban sewage and industrial effluents. NCTPS withdraws cooling water from the creek and disposes of warm water into sea through a pipeline. NCTPS draws cooling water from Ennore port, and discharges the warm water into the creek through the Buckingham canal. The frequent closure of the Ennore mouth has resulted in insufficient tidal inflow and thus reduced cooling waters for the thermal power stations. The Buckingham Canal area is prone to both point and non-point sources of pollutants. Raw municipal sewage, industrial trade effluents and industrial cooling waters all of them make its way through Buckingham canal, enters into Ennore estuary and eventually drains into the Bay of Bengal of Chennai coast (Usha Natesan and Ranga Rama Seshan, 2010). To identify the distribution patterns of major and trace metals in the sediments from Buckingham Canal (Jeyaprakash *et al.* 2012). If the assimilating capacity of the water body is not exceeded, the ecosystem is able to recover from additional stresses without permanent damage (Muthuraj and Jeyaprakash 2007). The mixing and transport process in the creek is highly dependent on the tidal ebbing and flooding conditions. The rapid development of Chennai City in the last two decades has polluted the creek and put additional stress on the local aquatic environment.

2.2. Sample Collection

Surface water samples (27) were collected (9 samples in each seasons) using separate polythene bottles for nutrients and Total suspended solid (TSS), and in glass stopper bottles for the estimation of Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) during three monitoring programs in pre-monsoon, monsoon and post-monsoon seasons during 2011 and 2012. Collected samples were stored in ice till they were transported to the deep freezer in the laboratory within 24 hours. The sampling sites covered the entire water spread area covered mostly with slushy conditions and the sites were selected on the basis of local input and the point sources, so that we can identify the possible source of input. Water samples were analyzed for various physico-chemical parameters based on the procedures described in (Grasshoff *et al.*, 1983; Parson’s *et al.*, 1984; APHA, 1995).Temperature, pH and salinity were measured using in situ. The filtered sample using 0.45 µm filter paper and dried at 103-105ºC and weighed for TSS (APHA, 1995). Analyses of dissolved nitrite (NO_2^-), nitrate (NO_3^-), Ammonia nitrogen (NH_4^+), in organic phosphates (IP), Total Phosphates (TP) and Total Nitrogen (TN) were determined using spectrophotometer procedures described by Parson’s et al 1984. DO and BOD concentrations were determined using Winkler’s titrimetric methods (Grasshoff *et al.*, 1983).

2.3. Multivariate Statistical Analysis (MSA)

All mathematical and statistical computations were made using SPSS Statistics Software. Multivariate analysis on the creek water quality data set was performed using Correlation analysis, Factor analysis and Cluster analysis techniques.

Correlation analysis is a helpful tool to see the relationships between numerical variables. Correlation coefficient ranges from -1 to +1. A correlation close to +1 indicates a direct relationship between two variables. A correlation close to -1 indicates an inverse relationship between the reflectance values of one variable and the reflectance values in the other one (Balasankar and Nagarajan, 2000). Factor analysis is one of the powerful techniques used for reducing the dimensionality of large datasets without loss of information (Wunderlin *et al.*, 2001). The factor loadings were sorted according to the criteria of (Liu *et al.*, 2003), i.e. strong, moderate and weak, corresponding to absolute loading values of

>0.75, 0.75-.50 and 0.50-0.30, respectively. Cluster analysis is defined as the classification of similar objects into groups where the number of groups as well as their forms are unknown (Kaufman, 1990), with the primary purpose being assembly of objects based on the characteristics they possess. Hierarchical agglomerative cluster analysis (CA) was performed on the normalized dataset. The dendrogram generated in CA provides a useful graphical tool in determining the number of clusters which describe underlying process that leads to spatial variation (Yang *et al.*, 2010).

3. Results and Discussions

3.1. Correlation Analysis

The basic statistics calculated for the creek water qualities are summarized in Table 1.

Table1: Descriptive statistics of seasonal variations of physico-chemical parameters.

	WT	pH	Salinity	DO	BOD	TSS	NO_2^-	NO_3^-	NH_4^+	TN	IP	TP
Pre-monsoon												
Min.	28.5	7.3	0.4	0.72	0.65	3	0.15	18.85	9.89	55.68	0.47	6.30
Max.	34.7	8.77	32.4	7.75	37.2	63.97	17.01	102.00	146.67	486.36	27.98	96.71
Mean	30.59	8.04	17.48	5.23	6.2	23.37	6.87	54.7	70.86	216.8	13.91	45.76
SD(±)	±1.95	±0.43	±12.85	±2.18	±11.87	±18.51	±6.08	±31.74	±50.57	±138.88	±11.74	±33.2
Monsoon												
Min.	29.5	7.9	0.3	2.3	0	8.8	1.1	6.5	3.2	24.8	0.32	12
Max.	33.8	8.5	35.1	5.7	33	85	18.3	85	133.2	312.5	24	95
Mean	31.12	8.18	19.44	4.46	10.94	30.76	7.56	34.19	60.73	149.42	8.18	49.54
SD(±)	±1.14	±0.22	±15.25	±1.26	±13.11	±26.3	±5.9	±27.64	±59.09	±111.48	±8.79	±29.49
Post-monsoon												
Min.	26.3	7.18	0.2	1.8	0	5.1	5.1	21.24	7.92	58.12	1.89	10.22
Max.	33	8.38	30.3	7.12	71	78	49.2	111	135	398.7	45.9	99.5
Mean	28	7.78	17.04	5.06	18.83	32.04	19.53	57.4	71.75	214.22	16.81	51.35
SD(±)	±1.2	±0.36	±12.33	±1.84	±25.46	±21.22	±14.51	±33.83	±49.14	±118.4	±15.36	±34.67

{(Units WT, temperature (°C); S, Salinity (%); DO, BOD and TSS (mg l^{-1}); NO_2^-, NO_3^-, NH_4^+, TN, IP and TP (µmol l^{-1})}

The water quality trend is inferred by correlation analysis. The seasonal correlation analysis of 12 variables is given in Table 2. NH_4^+ is positively correlated with NO_3^- in a moderate way during pre-monsoon, negatively correlated with pH in a strong way during pre-monsoon and post-monsoon. A moderate positive correlation of TN with TP and IP and strong positively correlated with BOD in all monsoons. TP is moderate positively correlated with TSS in monsoon season. BOD is negatively correlated with DO in all monsoons, positively correlated with TSS, NO_3^-, NH_4^+, TN, IP and TP during monsoon. It indicates the dilution of organic load due to monsoon and oxidation during pre-monsoon (Kathiravan *et al.*, 2014). A strong positive correlation with NH_4^+ during pre-monsoon and post-monsoon exists. It is found that a strong linear relationship exists between some of the variables from the correlation analysis.

3.2. Factor Analysis: Pre-monsoon

Factorial analysis was applied to 12 variables measured at the nine stations during pre-monsoon, monsoon and post-monsoon (Table 3, 4 & 5). A total of four significant factors observed during the pre-monsoon season are represented in Table 3. Factor 1 has a strong positive loading on IP. The high concentration of IP in the water mostly can be attributed to the human activities (Purvaja and Ramesh, 2000). It is well known that, IP are mostly derived from domestic sewage, agricultural effluents and industrial waste waters (Mohan Raj *et al.*, 2013). Factor 2 has a strong positive loading on BOD and TN. The high concentration of BOD in the water mostly derived from industrial effluents, agricultural runoff and discharge of untreated waste water from treatment plant (ICMAM, 2004). BOD and TN levels are high, DO levels decrease because the oxygen that is available in the water is being consumed by the bacteria. Since less DO is available in the water, fish and other aquatic organisms may not survive (Raffaell, 2000).

Table 2: Seasonal correlation coefficient between the physico-chemical parameters.

Pre-monsoon

	WT	pH	Salinity	DO	BOD	TSS	NO_2^-	NO_3^-	NH_4^+	TN	IP	TP
WT	1.00											
pH	-0.26	1.00										
Salinity	0.62	-0.31	1.00									
DO	-0.06	0.43	0.40	1.00								
BOD	0.01	-0.38	-0.41	-0.86	1.00							
TSS	-0.39	-0.51	-0.26	-0.56	0.25	1.00						
NO_2^-	0.45	-0.55	0.54	0.03	-0.32	0.29	1.00					
NO_3^-	0.00	-0.52	0.09	0.12	-0.19	0.22	0.49	1.00				
NH_4^+	0.38	-0.86	0.16	-0.52	0.40	0.36	0.51	0.67	1.00			
TN	0.21	-0.66	-0.16	-0.80	0.81	0.31	0.01	0.29	0.82	1.00		
IP	0.53	-0.31	0.34	-0.16	0.39	-0.48	-0.02	0.18	0.52	0.61	1.00	
TP	0.24	-0.57	0.26	-0.20	0.29	-0.07	0.12	0.60	0.77	0.72	0.82	1.00

Monsoon

	WT	pH	Salinity	DO	BOD	TSS	NO_2^-	NO_3^-	NH_4^+	TN	IP	TP
WT	1.00											
pH	-0.63	1.00										
Salinity	-0.82	0.89	1.00									
DO	-0.56	-0.07	0.00	1.00								
BOD	0.62	0.10	-0.15	-0.87	1.00							
TSS	-0.07	0.74	0.50	-0.55	0.72	1.00						
NO_2^-	-0.15	0.79	0.66	-0.57	0.43	0.73	1.00					
NO_3^-	0.15	0.59	0.41	-0.82	0.83	0.91	0.82	1.00				
NH_4^+	0.65	-0.16	-0.34	-0.72	0.92	0.55	0.07	0.61	1.00			
TN	0.48	0.17	-0.07	-0.77	0.97	0.79	0.37	0.82	0.94	1.00		
IP	0.12	0.62	0.45	-0.82	0.79	0.89	0.87	1.00	0.54	0.76	1.00	
TP	0.33	0.39	0.27	-0.94	0.85	0.76	0.78	0.96	0.63	0.78	0.96	1.00

Post- monsoon

	WT	pH	Salinity	DO	BOD	TSS	NO_2^-	NO_3^-	NH_4^+	TN	IP	TP
WT	1.00											
pH	0.12	1.00										
Salinity	0.65	-0.34	1.00									
DO	0.12	0.68	0.18	1.00								
BOD	-0.36	-0.74	-0.26	-0.73	1.00							
TSS	-0.51	-0.68	-0.17	-0.47	0.57	1.00						
NO_2^-	-0.44	-0.30	-0.34	-0.33	0.28	0.81	1.00					
NO_3^-	-0.42	-0.47	0.31	0.17	0.06	0.65	0.41	1.00				
NH_4^+	-0.20	-0.95	0.35	-0.65	0.65	0.56	0.25	0.47	1.00			
TN	-0.46	-0.78	-0.19	-0.89	0.81	0.60	0.36	0.16	0.82	1.00		
IP	-0.42	-0.88	0.03	-0.64	0.67	0.93	0.64	0.63	0.81	0.78	1.00	
TP	-0.41	-0.87	0.19	-0.61	0.53	0.77	0.44	0.66	0.90	0.80	0.93	1.00

TN can be attributed to seepage of effluents from fertilizer industries and the solid waste dumped in the canal. Factor 3 has a strong positive loading on temperature, salinity and moderate positive loading on Nitrite. The high level temperature in the water is mostly derived from NCTPS discharges of 27.5m^3/s of condenser reject water at about 5 °C to 8 °C above ambient temperature (Buvaneshwari *et al.*,2014). The high concentration of salinity is attributed by the accumulation of flood tide water in the salt pans of the upstream areas. Salinity acts as a limiting factor in the distribution of living organisms, its variation caused by dilution and evaporation which influence the characteristic change of fauna in the intertidal zone (Gipson, 1982). Factor 4 has a strong positive loading on Nitrate, and moderate positive loading on NH_4^+ and TP. This factor represents the effect of municipal sewage and fertilizer waste. According to Meybeck (1990), animal wastes and fertilizers make a much greater contribution to nitrogen pollution. High concentration of ammonia present in water may be toxic to aquatic organisms. Ammonia is present in terrestrial and aquatic environments. Plants and animals excrete ammonia; it is produced by the decompositions of organisms and by the activity of microorganisms (Prosser and Embley, 2002).

Table 3. Results of factor analysis during pre-monsoon season.

Variables	Factor 1	Factor 2	Factor 3	Factor 4
WT	0.35	0.15	0.86	-0.03
pH	0.23	-0.47	-0.41	-0.65
Salinity	0.20	-0.31	0.83	0.13
DO	0.21	-0.96	0.04	-0.02
BOD	0.13	0.95	-0.18	-0.02
TSS	-0.84	0.38	-0.11	0.27
NO_2	-0.42	-0.13	0.73	0.42
NO_3	-0.08	-0.17	0.01	0.95
NH_4	-0.01	0.52	0.33	0.78
TN	0.18	0.86	0.01	0.48
IP	0.81	0.35	0.27	0.35
TP	0.51	0.29	0.01	0.78
Eigen value	4.93	2.93	2.10	1.24
%Total variance	41.12	24.42	17.47	10.35
Cumulative %	41.12	65.53	83.01	93.36

Table 4: Results of factor analysis during monsoon season.

Variables	Factor 1	Factor 2
WT	0.59	-0.74
pH	0.13	0.97
Salinity	-0.08	0.97
DO	-0.92	-0.03
BOD	0.99	-0.06
TSS	0.72	0.59
NO_2	0.50	0.77
NO_3	0.87	0.49
NH_4	0.89	-0.31
TN	0.95	-0.00
IP	0.84	0.54
TP	0.91	0.33
Eigen value	7.46	3.60
%Total variance	62.12	30.03
Cumulative %	62.12	92.15

3.3. Factor analysis: Monsoon

Two significant factors observed during the monsoon season are represented in Table 4. Factor 1 has a strong positive loading on BOD, TN, TP, NH_4^+, NO_3^- and IP and moderate positive loading on TSS. Factor 2 has a strong positive loading on salinity and pH and moderate positive loading on NO_3^-.

3.4. Factor analysis: Post monsoon

A total of three significant factors observed during the post monsoon season are represented in Table 5. Factor 1 has a strong positive loading on pH and moderate strong positive loading on DO. Factor 2 has a strong positive loading on salinity. There is no considerable positive loading representing Factor 3. Based on the factor analysis, it is observed that factor 1 is dominant during the monsoon season which is attributed due to partially opening of the mouth (50-75m wide). This opening is relatively smaller when compared to pre and post-monsoon width of 200 m & 110 m respectively (Jebakumar *et al.*, 2014). The maximum enrichment of nutrients occurs during monsoon season when compared to pre and post due to the precipitation of pollutant (Kathiravan *et al.*, 2014).

Table 5: Results of factor analysis during post-monsoon season.

Variables	Factor 1	Factor 2	Factor 3
WT	0.47	0.68	0.27
pH	0.90	-0.39	-0.11
Salinity	0.03	0.98	-0.19
DO	0.73	0.05	-0.62
BOD	-0.76	-0.15	0.44
TSS	-0.87	-0.21	-0.33
NO_2	-0.58	-0.44	-0.36
NO_3	-0.53	0.19	-0.80
NH_4	-0.87	0.40	0.11
TN	-0.89	-0.09	0.39
IP	-0.97	0.03	-0.15
TP	-0.93	0.21	-0.14
Eigen value	6.90	2.09	1.792
%Total variance	57.46	17.40	14.93
Cumulative %	57.46	74.87	89.80

3.5. Cluster analysis-Dendrograms

Dendrograms were generated which grouped the sampling sites based on the values of physico-chemical parameters in three seasons (Fig.3) and the mean values of physio-chemical constituents for each cluster are shown in Fig.2. Cluster analysis generated three clusters during pre-monsoon. Cluster 1 comprised of EKRR and EAMC; cluster 2- WQE 5, EBUCS, EBUCN, WQE 4, WQE 3 and WQE2; cluster 3- WQE1. Similarly ,during monsoon, it generated three clusters; cluster 1- EKRR; cluster 2- EAMC; cluster 3- EBUCN, EBUCS, WQE5, WQE4, WQE3, WQE2 and WQE1;For the post-monsoon it generated three clusters; cluster 1- EKRR and EAMC; cluster 2- EBUCS, EBUCN, WQE5, WQE4, WQE3 and WQE2;cluster 3- WQE1; These differences are mainly due to the inflow- outflow characteristics and the resulting circulation pattern taking place within the creek(Fig 1 c).

It was observed that pre-monsoon cluster II-stations WQE 5, EBUCS, EBUCN, WQE 4, WQE 3 and WQE2, monsoon cluster III- stations EBUCN, EBUCS, WQE5, WQE4, WQE3, WQE2 and WQE1 and post-monsoon cluster II- stations EBUCS, EBUCN, WQE5, WQE4, WQE3 and WQE2 are having higher concentration in WT, BOD , NO_3^-, NH_4^+ , TN, IP and TP. During pre-monsoon and post-monsoon, cluster stations are the same where as in monsoon there is one more station (WQ1) has included, because of mouth closure during the monsoon season, station WQ1 registers higher pollution (Jebakumar *et al.*,2014). These cluster stations are all located at north and north east part of the Ennore estuary (Fig 1c).where, Buckingham canal is contributing Raw municipal sewage, industrial trade effluents (Usha Natessan *et al.*, 2010; Jeyaprakash *et al.* 2012) and discharge of NCTPS coolant water in Stations EBUCS, WQE4 and WQE5.Significant input of fecal coliform also occurs from the Buckingham canal (Buvaneshwari *et al.*, 2014; Jebakumar *et al.*, 2014).

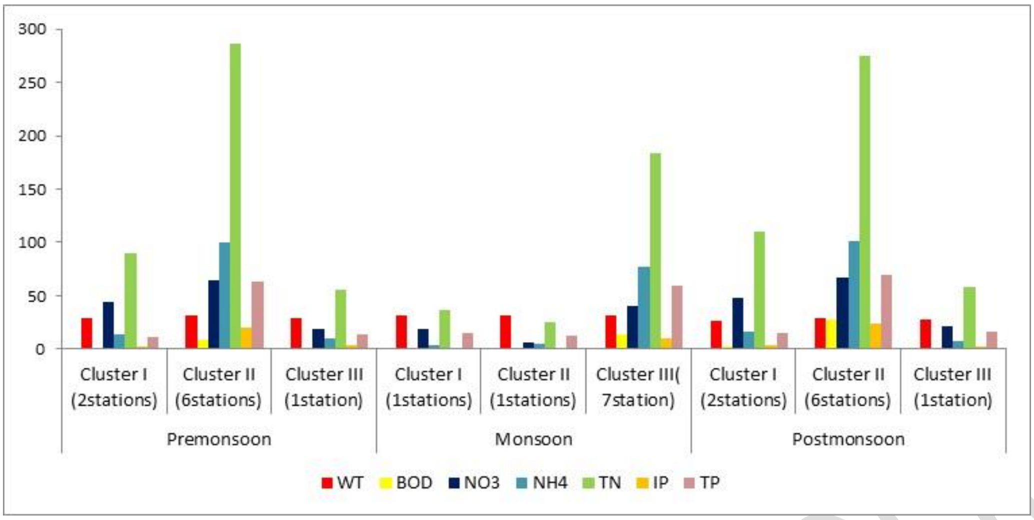

Figure 2.Mean values of physico-chemical constituents for each cluster

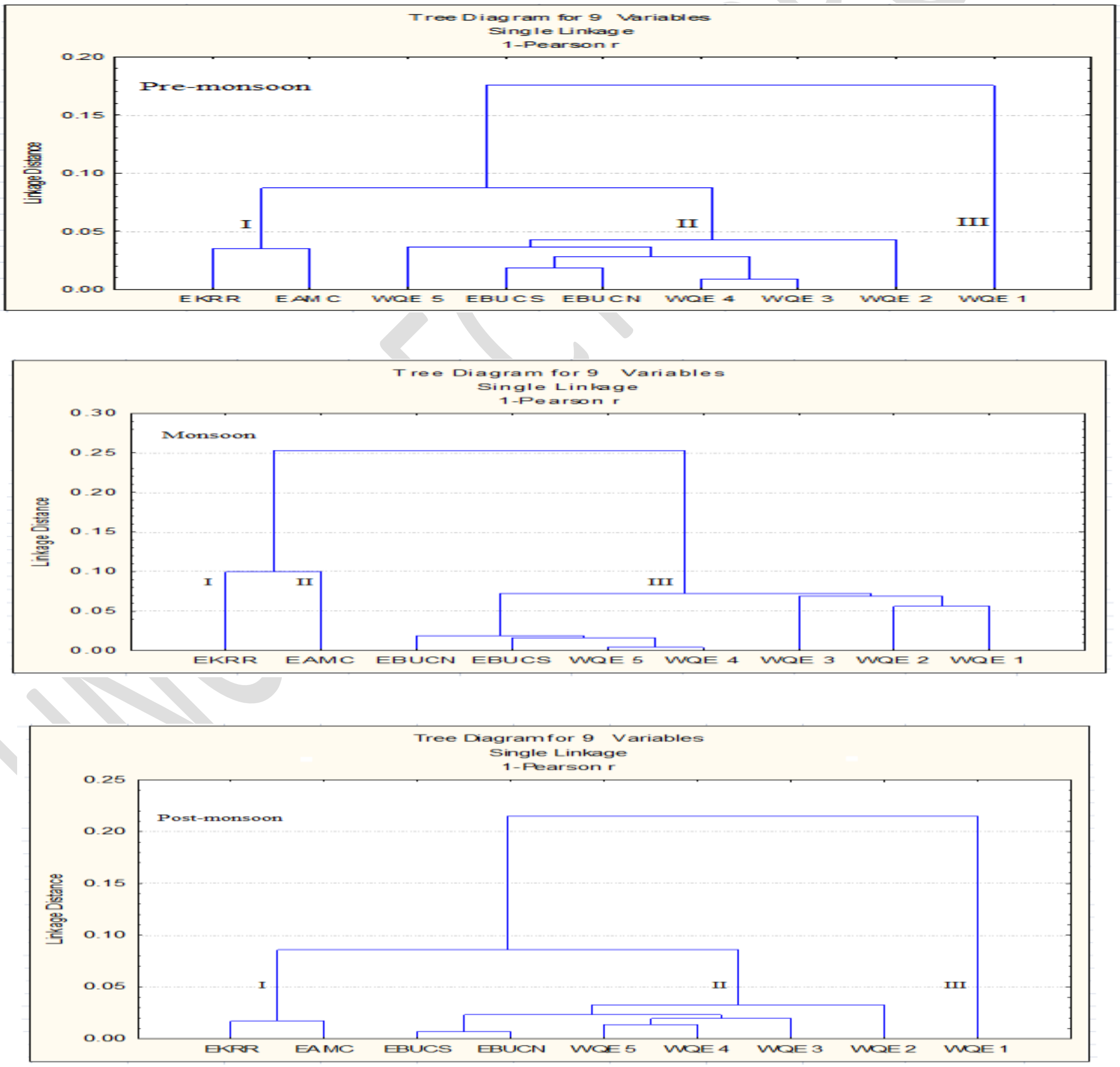

Figure 3. Dendogram based on clustering method for pre-monsoon, monsoon and post-monsoon seasons.

4. Conclusions

The present study summarizes the seasonal fluctuations in various physiochemical parameters in the Ennore creek as an exploratory statistical data output. Based on the factor analysis, it is observed that factor 1 is dominant during the monsoon season which is attributed due to partially opening of the mouth (50-75m wide). This opening is relatively smaller when compared to pre and post -monsoon width of 200 m & 110 m respectively. The maximum enrichment of nutrients occurs during monsoon season when compared to pre and post due to the precipitation of pollutant. Results of cluster analysis show that pre-monsoon cluster II, monsoon cluster III and post-monsoon cluster III are having highest concentration in WT, BOD, NO_3^-, NH_4^+ , TN, IP and TP. Among these cluster stations, EBUCS, WQE 4 and WQE5 are in direct contact with Buckingham canal source and NCTPS coolant water. This study illustrates the usefulness of multivariate statistical techniques in the analysis and interpretation of complex data sets, in identifying pollution sources and in understanding variations in water quality for effective creek water management and future planning.

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{(Abbreviations EKRR- Ennore Creek Kortalliyar River; EAMC-Ennore Creek Amullavoyal Canal; EBUCS-Ennore Creek Buckingham Canal South; EBUCN-Ennore Creek Buckingham Canal North; WQE5-Ennore Creek D/S of Kosasthalaiyar river junction; WQE4 -Ennore Creek D/S of Amullavoyal junction ; WQE3- Ennore Creek D/S of Kortalliyar river junction; WQE2- Ennore Creek south of railway bridge; WQE1- Ennore Creek mouth(100m inside))}

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